# Charge Carrier Localisation in Metal Halide Perovskites for Optoelectronic Applications



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This thesis is submitted for the degree of Doctor of Philosophy September 2020

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Sascha Feldmann
 September 2020

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### Sascha Feldmann

This dissertation is concerned with the charge carrier dynamics in semiconductors based on metal-halide perovskites. These materials have shown remarkable performance in optoelectronic applications like solar cells or light-emitting devices. They are solution-processable at low temperature using inexpensive earth-abundant reagents, have low Urbach energies, high carrier mobilities and long diffusion lengths, while their bandgap can be tuned across the visible and near-infrared spectrum through the chemical composition.

In this thesis, two different perovskite-based systems are studied with respect to their carrier dynamics and related photoluminescence yields as a probe for their performance in devices.

The first study compares a variety of perovskite thin films containing mixed cations (cesium, methylammonium, formamidinium) and mixed halides (bromide, iodide). I find that the disordered energetic landscape arising from domains that are bromide- or iodide-rich allows charge carriers to accumulate in low-bandgap regions. Recombination of charges at these sites follows quasi-first-order kinetics and the locally high carrier density allows bimolecular radiative recombination to outcompete trap-mediated loss channels. Thus, the photoluminescence yields in mixed-halide compositions remain high even at low excitation densities. This unearths a new route towards highly efficient light-emitting devices or solar cells through micro-structuring of the energy landscape in these materials.

The second study investigates the consequences of manganese-doping for the carrier dynamics of cesium lead halide nanocrystals. Photoluminescence quantum yields are shown to double upon doping. This is found to be not only a consequence of reduced non-radiative losses, but of an increased intrinsic radiative excitonic recombination rate as well. The origin of this stronger emission lies in a carrier localisation effect induced by the manganese dopants which locally break the periodicity of the host crystal lattice. This leads to an increased overlap of electron and hole wave functions and thus favours radiative recombination. The mechanism provides a new strategy of transition-metal doping for highly efficient light-emitting devices.

### to Shila,

and to those who will not have the benefit of about two billion years' accumulated energy reserves

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### **Chapter 1: Introduction**

The Earth is getting hotter. This is a statement unambiguously supported by evidence based on the scientific method, and not an opinion.

This matter is of such importance that I shall start the introduction of this PhD thesis bluntly with a graph. Figure 1 summarises data from the United States National Aeronautics and Space Administration (NASA) and shows that the Earth is gradually heating up since the beginning of the 20<sup>th</sup> century.



Figure 1: Global temperature anomaly. The Lowess-based smoothing uses a 10-year running mean. Data is based on the National Aeronautics and Space Administration (NASA) Goddard Institute for Space Studies as of September 2020.

The month May 2020 was about 1.5°C hotter than the average month recorded on Earth since 1880. The Earth's climate is changing, after more than 10,000 years of relative stability – this is the full span of human civilisation. With the rising average temperatures, acute hazards such as heat waves and floods grow in both severity and frequency, while chronic hazards such as drought and rising sea levels greatly intensify [1]. Not only is climate change already now having a substantial physical impact at a local level in regions across the world; the socioeconomic impact of it will likely rise non-linearly, as system thresholds are breached and

have knock-on effects. To give a concrete example: as heat and humidity will increase in India, already by 2030 (under a representative  $CO_2$  concentration pathway of 8.5 scenario) between 160 and 200 million people could live in regions with an average 5% annual probability of experiencing a heat wave that exceeds the survivability threshold for a healthy human being, absent an adaptation response [2].

It is obvious that unless we dramatically change our global energy supply from mostly relying on fossil fuels to renewable energy forms, supported by an active decarbonisation strategy, we will fail to adhere to the long-term goal to keep the increase in global average temperature well below 2°C above pre-industrial levels, as set out by the Paris Agreement [3] under the United Nations Framework Convention on Climate Change in 2015/2016.

As of 2018, renewable energy sources represented 18.9% of the total energy consumption in the European Union, on a path to the 2020 target of 20% [4,5]. Yet, there is a wide spread in the energy consumption for individual member states: While Sweden reached a share of 54.6% of gross final energy consumption from renewables in 2018, in Germany this value is only a fraction of that at 16.5%, similar to the United Kingdom at 11.0%; the Netherlands reached only 7.4%. None of these states are considered particularly poor in a European or global context, indicating that a transition towards renewable energy production is also highly driven by geopolitical factors.

One of these 'renewables' – among wind power, biomass, geothermal or hydropower is solar energy. It is truly remarkable that our sun, essentially a large nuclear fusion reactor, transmits enough energy to the Earth every hour to meet the world's energy demand for a whole year [6]. Therefore, it would make sense to 'reach for the stars' and try to exploit this abundant energy source, for example using the photovoltaic effect in a solar cell to produce electricity. However, if we consider the current market situation, for example, in Germany, then we find that while the country generated about 46% of their public electricity from renewables in 2019, only 9% was based on solar energy [7,8] – so what is holding this technology back?

It is mainly the cost-effectiveness: the total price paid for fabricating a solar cell, installing and maintaining it, while it either occupies land area or is integrated on roof tops. Most commercially available solar panels will be based on silicon, where power conversion efficiencies of >20% are readily available [9]. However, increasing their efficiencies only incrementally further, approaching the theoretical limit set out for a single-junction cell by Shockley and Queisser in 1961 [10], will imply much higher related costs. Another economically motivated approach would be to focus on mass production instead and thus lower the cost per module significantly, without making each one more efficient. However, in this

scenario we would soon be sacrificing a significant fraction of the available area, without meeting the energy goals set. The heaviness, complex manufacture and inherent inflexibility of silicon-based photovoltaics as a result of their indirect bandgap and weak optical absorption that make thick layers necessary, act like a cap on the widespread uptake of solar cells.

Solution-processable semiconductors could overcome these limitations, be manufactured to be thin and flexible through cheap roll-to-roll or spray-on processing, which could make these products accessible particularly in the developing world for the first time.

Metal-halide perovskites form such a material class and hold great promise for extremely high device efficiencies, now exceeding 25% in solar cells [9] at significantly reduced production costs – thus greatly increasing the cost-effectiveness of solar cells, while also enabling portable light-weight and flexible applications. This disruptive technology requires condensed matter physicists, materials chemists and device engineers to work hand in hand in order to overcome existing challenges, for example, the stability of these materials, while pushing the boundaries of power conversion efficiencies even further towards their fundamental limit.

Many of the underlying physical properties of perovskites that led to the revolution in solar cells also enable enhancements in the performance of light-emitting devices (LEDs), for example an absorption coefficient that surpasses that of gallium arsenide – a leading semiconductor in high-performance commercial optoelectronic devices like solar cells, LEDs or lasers.

Aside from increasing the fraction of energy produced from renewable sources, another strategy to limit climate change would be to reduce the global energy demand. However, the world's population is still growing, and an increasing number of developing countries are expected to gain more access to high-end technologies. Thus, the global energy consumption is expected to increase rather than decrease in the upcoming decades. A large fraction of this energy demand stems from telecommunication, lighting and display technologies. Therefore, a promising strategy is to focus on increasing the efficiency of these applications, as their global availability rises [11].

As such, conducting research in a class of novel semiconductors like perovskites, that are promising for both solar cells and as photonic sources, appears to be a useful strategy to help limiting climate change. This represents, together with the curiosity of understanding fundamental physical processes, the main driver for my work summarised in this PhD thesis. In the following chapters, we will first review in Chapter 2 the basic concepts of semiconductor physics, their application in optoelectronic devices, and summarise the fundamental properties

of the metal-halide perovskite materials family. Chapter 3 will then provide an overview of the methods used in the studies of this PhD thesis, with a focus on optical spectroscopy.

In Chapter 4, a study on alloyed perovskite thin films of varying composition will be presented. It was found that the energetic disorder present in these materials can indeed be beneficial for optoelectronic device performance, because it allows charges to accumulate in local regions of lower energy potential. In these regions of high carrier density, the radiative recombination outcompetes non-radiative losses, keeping the overall efficiency measured in terms of luminescence yield high – even at low excitation densities – promising for photovoltaic or LED applications that operate at solar illumination conditions or low currents.

Chapter 5 will summarise a study on metal-halide perovskites in the form of colloidal nanocrystals where spatial confinement influences the charge carrier dynamics significantly. These nanocrystals were doped with isovalent manganese ions, resulting in significantly enhanced photoluminescence quantum yields. Remarkably, these gains are not only a consequence of trap-passivation, as frequently assumed in the literature, but also result from an increased radiative excitonic recombination rate – an intrinsic material property that is generally hard to modify. The origin of this observation lies in the localisation of charges induced by the lattice periodicity breaking of the dopants, thus increasing the overlap of electron and hole wavefunctions which promotes radiative recombination. This finding unearths a new strategy for more efficient LEDs based on chemically tailored transition-metal localisation centres that could well be generalised beyond the specific case studied here.

Finally, in Chapter 6 I will summarise these results and draw conclusions from them for future research directions on the path towards a sustainable energy future.

### **Chapter 2: Theoretical Background**

In this chapter we will discuss the fundamental concepts which underlie the experimental studies which I carried out within the framework of my PhD. We will start with a brief overview on the basics of solid-state physics of semiconductors. We will then move on to the mechanisms involved in applications based on such semiconductors, namely for solar cells. Lastly, we will examine the structural and electronic properties of the material class of metal-halide perovskites, which I primarily studied during my PhD and which are the semiconductors discussed in this thesis. We will also briefly discuss the consequences of spatial confinement on the optoelectronic properties of semiconductors in general and for the case of perovskites, since such a nano-scale system will be object of the studies in Chapter 5.

### 2.1 Solid-state physics of inorganic semiconductors

Here, we shall review the fundamental solid-state physics of semiconductors, their electronic structure, occupation of charge carriers, and interaction with light, responsible for the optoelectronic properties investigated in this thesis. Most of the concepts explained here are - if not referenced otherwise – based on the books by Kittel [12], and Yu and Cardona [13], where derivations can be found in more detail.

#### **2.1.1 Band theory**

In order to understand the properties and behaviour of electrons in a crystalline semiconductor like silicon or GaAs, we first discuss the concept of *band formation* to describe these systems. We start with solving the Schrödinger equation for a periodic arrangement of atoms which form the crystal lattice, stated by the general Hamiltonian:

$$H = H_{nuc}(R_j) + H_e(r_i, R_{j,0}) + H_{nuc-e}(r_i, \delta R_{j,0})$$
(1)

where under the Born-Oppenheimer approximation [14] the much slower motion of the nuclei (and the time-averaged adiabatic electronic potentials) with the corresponding Hamiltonian  $H_{nuc}(R_j)$  can be separated from the much faster electronic motion with the corresponding Hamiltonian  $H_e(r_i, R_{j,0})$ , since the electrons experience the nuclei as being nearly static in their positions. The cross-term  $H_{nuc-e}(r_i, \delta R_{j,0})$  considers the change in electronic energy due to displacements  $\delta R_{j,0}$  of the ions from their equilibrium positions. In the 'mean field approximation', the electronic Hamiltonian can further be expressed such that each electron experiences the same periodic potential set out by the ions in the lattice V(r), yielding the simplified one-electron equation:

$$\left(\frac{p^2}{2m} + V(r)\right)\phi_n(r) = E_n\phi_n(r)$$
(2)

Here,  $\phi_n(r)$  is the electron wavefunction of an eigenstate *n*, and  $E_n$  the corresponding energy. According to Bloch's theorem [15], solutions of this equation can be written as a plane wave modulated by a periodic function:

$$\phi_{n,k}(r) = u_k(r) e^{i k r} \tag{3}$$

where  $\phi_{n,k}(r)$  is also called a Bloch wave of a given band index n, r is the electron's position,  $u_k(r)$  is a periodic function with the same periodicity as the crystal lattice, and k is the crystal momentum vector. A plot of the energy  $E_k$  versus the wave vector k yields what is called the electronic *band structure* of a given crystal, illustrated in Figure 2.



Figure 2: Band structure of a free electron. Here, the extended zone scheme is shown, whereas a reduced zone scheme would restrict the plotted wave vector k to its unique values given by the first Brillouin zone instead.

The possible k values are usually plotted over a range following certain symmetry directions along the crystal lattice, for example limited to  $[-\pi/a, \pi/a]$ . This is called the first *Brillouin* 

*zone* [16], which is a uniquely defined primitive cell within the reciprocal lattice, because following the translational symmetry of the crystal, the wave numbers k and  $k + (2\pi l/a)$ represent the same solution to the Schrödinger equation, with l as an integer and a as the crystal lattice constant of a primitive cell. For a lattice potential V(r) approaching zero, the free electron dispersion is retrieved, i.e.  $E \sim k^2$ , yielding a parabolic band. The electron waves traveling through the crystal will be reflected at the Brillouin zone boundaries, where the Bragg condition is fulfilled and electrons are reflected off the crystal layers, forming standing waves of the form:

$$\phi_+ = \cos\left(\frac{nx}{a}\right) \tag{4}$$

$$\phi_{-} = \sin\left(\frac{\pi x}{a}\right) \tag{5}$$

These two waves will have different corresponding energies, since they present electrons at different positions with respect to the crystal lattice, and hence electrons will experience a different potential depending on the distance to the ions in their proximity. For  $\phi_+$  electrons have the highest probability density at the positions of the nuclei, while for  $\phi_-$  they are most likely positions in between the ions of the lattice. Therefore, the  $\phi_-$  wave has higher potential energy than the  $\phi_+$  wave, and a plot of the two will result in an energy gap formed at the Brillouin zone boundary, which we call a bandgap (or forbidden band). Occupying these states with available electrons in the system starting with the lowest energy will in a semiconductor thus result in an occupied lower band, the valence band, and an unoccupied upper band, the conduction band. Within this picture, a semiconductor describes a material having a non-zero bandgap of below ~4 eV [17], above which it is more appropriate to use the term insulator.

Following this procedure, a band diagram can in principle be constructed, where with different sorts of atoms constituting a given lattice, a linear combination of the respective atomic orbitals (LCAO approach, LCAO: linear combination of atomic orbitals) involved will result in the same number of bands. This 'tight-binding' approach is similar to the formation of molecular orbitals from hybridisation of atomic orbitals to explain the chemical bonds in molecules.

Because the processes involving transitions of electrons near the bandgap are of the highest interest to explain many properties of semiconductors, the band structure is often approximated near the bandgap to be simply parabolic. By performing a Taylor expansion of E(k) around the conduction and valence band edges in powers of  $E(k - k_0)$ , we find:

**Chapter 2: Theoretical Background** 

$$E(k) = E(k_0) \pm \frac{\hbar^2 (k - k_0)^2}{2m^*}$$
(6)

Here, the positive and negative sign represents the case of the conduction and valence band, respectively, and the first-order (linear) term in the Taylor expansion vanished, since the first derivative at the band extrema  $(k_0)$  is zero. The result of this 'effective mass approximation' is almost identical to the free electron solution displayed earlier, with the only difference being a modified electron mass, which mathematically describes the band curvature. This effective mass  $m^*$  is meant to account for the complicated potential set out by the atomic nuclei experienced by an otherwise freely moving electron. This parabolic approximation will also be useful in the discussion of the electronic structure of nanocrystalline semiconductors below.

Notably, the conduction and valence band edges can be located either at the same position in k space, or at different positions, depending on the semiconducting material. In the former case, we speak of direct bandgap semiconductors, like for example GaAs, while in the latter we call them indirect, e.g. Si. The consequences for the optoelectronic properties of a material depending on the nature of the bandgap can be dramatic. As an example, the optical transitions considered in the next section are mediated by photons which carry a well defined yet very small momentum. Hence, in order for absorption or emission to take place between the band edges, in the case of an indirect bandgap, additional momentum contributions, usually in the form of phonons (lattice vibrations) are necessary – greatly reducing the probability of these processes and thus hampering the material performance in a solar cell or light-emitting device, where light absorption and emission are key.

### 2.1.2 Optical transitions

Now that we have derived the general electronic structure of a semiconductor, we will next discuss the interaction of this material class with electromagnetic radiation. In order to capture the most important phenomena relevant for describing the optoelectronic properties of the perovskite materials in this thesis, the model of light acting on an ensemble of dipole oscillators is often sufficient. Yet, a more comprehensive description will be based on quantum mechanics.

For the electronic transition rate  $\Gamma_{i \to f}$  between the initial state  $\Psi_i$  and the final state  $\Psi_f$  of an atom, or any two-level system with energies  $E_f$  and  $E_i$ , we can apply the formalism derived originally by Dirac [18] and termed 'Fermi's Golden Rule':

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \left\langle \Psi_f \left| H' \right| \Psi_i \right\rangle \right|^2 \rho_f(E)$$
(7)

Here, the term in brackets describes the matrix element

$$\mathbf{M}_{i \to f} = \left\langle \Psi_f \left| H' \right| \Psi_i \right\rangle \tag{8}$$

of the perturbation Hamiltonian due to the presence of an oscillating light field, and  $\rho_f(E)$  is the density of final states (needed when considering a manifold of states, such as in a band-like semiconductor). The Hamiltonian can also be written as

$$H' = -p \cdot E = -e \ r \cdot E \tag{9}$$

where p is the electric dipole moment operator of the electron and E is the electric field of the light incident on the system. If the interaction Hamiltonian is oscillating at an angular frequency  $\omega$  and can be described as interacting with the system adiabatically, then the transition rate becomes:

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \mathsf{M}_{i \to f} \right|^2 \left[ \delta \left( E_f - E_i - \hbar \omega \right) + \delta \left( E_f - E_i + \hbar \omega \right) \right]$$
(10)

Neglecting any rapidly oscillating terms, only transitions with the same energy as that of a photon  $\hbar\omega$  can conserve energy and is thus an allowed transition. In the case of a positive energy difference this corresponds to light absorption, and in the negative case to stimulated emission. The spontaneous emission is more complicated to derive via quantum electrodynamics, but can be recovered from Einstein relations between the  $A_{21}$ ,  $B_{21}$  and  $B_{12}$  coefficients describing spontaneous emission, stimulated emission and absorption, respectively [19]. We see that under the given approximations, the matrix element which characterises the electronic transition strength is dependent only on the electric dipole moment – a fundamental material property – and the strength of the incoming electric field of the light. In chapter 5, we shall see how excitation localization through dopants can act as a perturbation to increase the fundamental radiative transition rate in a semiconductor that I observe.

Within the framework of this theory, only transitions that conserve the total momentum in the system are allowed. Since photons in the UV-visible spectrum have much smaller momentum than electrons in the Brillouin zone typically do [20], optical transitions considered here lead to negligible changes in the wavevectors of electrons, and thus photon absorption or emission processes discussed in this thesis are generally considered 'vertical transitions', referring to no change in k in a band diagram. Indirect transitions, as mentioned above for the case of indirect

semiconductors, generally need to be assisted by lattice vibrations, balancing the momentummismatch through either creation or destruction of the necessary quanta of phonons in addition to that of a photon. As a consequence, indirect bandgap materials like silicon generally require thick layers of about 1 mm in order to absorb a significant part of the incoming sun light, whereas direct semiconductors like GaAs (or likely metal-halide perovskites) require only hundreds of nanometres of thickness, allowing for thin-film and flexible applications in solar cells and related technologies.

### 2.1.3 Occupation of bands

After we have successfully established the electronic structure of bands in semiconductors, we will next discuss to what extent the individual ensembles of available states are occupied by electrons of a given energy. Within the framework of this thesis, we are heavily concerned with the behaviour of charge carriers upon excitation with light, and track these carrier dynamics with time-resolved absorption and emission experiments.

Since electrons are fermions, their distribution in a manifold of states will follow Fermi-Dirac statistics [21,22], when in thermodynamic equilibrium. The temperature-dependent probability of finding an electron with energy E is:

$$f(E, E_F, T) = \frac{1}{e^{E - E_F/k_B T} + 1}$$
(11)

Here,  $E_F$  is the Fermi level, i.e. the energy level at which in thermodynamic equilibrium an electron would have a 50% probability to occupy this energy level at any given time, and  $k_B$  is the Boltzmann constant. Note that in contrast the Fermi *energy* is defined as the energy value of the highest single-particle state occupied by an electron in a metal at absolute zero (0 K). Under the 'Boltzmann approximation', i.e. if the Fermi level is far away from both the valence and conduction band edges, e.g. at half the bandgap energy, the resulting conduction band occupation is:

$$f_c(E, E_F, T) \approx e^{(E_F - E)/k_B T}$$
(12)

and the corresponding valence band occupation is then:

$$f_{\nu}(E, E_F, T) = 1 - f_c(E, E_F, T) \approx e^{(E - E_F)/k_B T}$$
 (13)

Thus, the number of electrons in the conduction band n, and the number of holes in the valence band p, are given by:
$$n = N_c e^{E_F - E_c/k_B T} \tag{14}$$

and

$$p = N_v e^{E_v - E_F/k_B T}$$
<sup>(15)</sup>

with the effective density of states of the conduction and valence band:

$$N_{c,\nu} = 2 \left( \frac{m_{c,\nu} k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}}$$
(16)

From this, the *intrinsic carrier density*  $n_i$  (as well as the ideal dark current equation), which is an intrinsic material property, can be directly derived as:

$$n p = n_i^2 = N_c N_v \, e^{-E_g/k_B T} \tag{17}$$

This relation is also referred to as 'law of mass action' and states that, regardless of doping, the product of electron and hole densities is a constant at equilibrium, which only depends on the bandgap  $E_g$  and the temperature of the material.

## 2.1.4 Exciton formation

We shall next briefly discuss the quasi-particle arising from electron-electron interactions not generally considered in the band theory described above, called an *exciton*. It should be noted that other interaction terms like exchange and correlation effects will not be discussed in detail here, but add to the complexity of describing optical spectra quantitatively.

The Coulombic attraction between a negatively charged electron, e.g. excited in the conduction band, and the positively charged hole, for example the vacancy left in the valence band upon excitation, causes the electron and hole motion to be correlated. The resulting electron-hole pair is called an exciton and the total energy of the system is thus reduced compared to the separate electron and hole energies.

It is useful to distinguish two extreme scenarios of such an exciton, depending on the strength of electron-hole interaction. In the limit of a *Frenkel exciton* [23], the correlated pair is highly localised to within one or two unit cells of an ionic crystal, or a single molecule. In the other limiting case, the electron-hole pair is only weakly bound, such that electrons and holes are delocalised over a large number of crystalline unit cells – termed *Wannier-Mott excitons* [24]. The latter case requires large dielectric constants in the medium enabling effective charge screening.

Wannier-Mott excitons can be well described within the previously used effective mass approximation, where the exciton is treated as hydrogen-atom-like (though a positronium would be the more appropriate analogue given the more similar masses compared to a proton and an electron). Solving the Schrödinger equation in this case yields the same energy quantisation as the atomic orbitals, with energy levels:

$$E_b(n) = -\frac{\mu^* R_H}{m_0 \varepsilon_r^2 n^2} \tag{18}$$

with the reduced effective mass  $\mu^* = m_e^* m_h^* / (m_e^* + m_h^*)$ , the hydrogen atom Rydberg constant  $R_H$  (13.6 meV), the electron rest mass  $m_0$  (9.11×10<sup>-31</sup> kg), the dielectric constant of the material  $\varepsilon_r$  and the integer principal quantum number n. This energy can now be understood in the context of an exciton *binding energy*, where the stronger Coulombic attraction is considered in a higher reduced effective mass of the electron and hole.

Similar to the hydrogen atom Bohr radius  $a_B$ , we can also define the exciton Bohr radius  $a_X$  which follows the same discrete 'orbits', i.e. quantisation in n:

$$a_X = \frac{m_0 \varepsilon_r n^2 a_B}{\mu^*} \tag{19}$$

The exciton binding energy and radius are the most common quantities to describe the strength of electron-hole interactions. As a typical example of weakly bound excitons, in crystalline GaAs with a dielectric constant of 12.8, and effective electron and holes masses of 0.067 m<sub>0</sub> and 0.2 m<sub>0</sub>, respectively, we find an exciton binding energy of 4.9 meV and a radius of 11 nm [25]. Thus, at room temperature (i.e. thermal energy of  $k_BT\sim25$  meV) mostly free charge carriers are present in the system.

However, it should be noted that while often the exciton energy levels are shown superimposed on a one-electron energy band structure, this is an incorrect representation given the two-article nature of these states. Instead, it is useful to first decompose the exciton motion into two parts: the centre of mass motion, and the relative motion of the electron and hole about their centre. Thus, the potential acting on the exciton centre of mass maintains translational invariance since the Coulomb interaction depends only on the relative coordinate of the electron and the hole. Then, the exciton wave vector *K* can be shown to be the sum of the electron  $k_e$  and hole  $k_h$ wave vectors according to

$$K = k_e + k_h \tag{20}$$

which is a better suited quantum number to describe the state. It is then related to the exciton energy  $E_X$  (and not only its binding energy compared to the free particle from above) via:

$$E_X = \frac{\hbar^2 K^2}{2m_e + m_h} \tag{21}$$

The corresponding exciton wave function is best described as a Wannier function, which for a perfect crystal lattice yields:

$$\phi_R(r) = \frac{1}{\sqrt{N}} \sum_k e^{-i \, k \cdot R} \psi_k(r) \tag{22}$$

with the Bloch functions  $\psi_k(r)$ , N as the number of primitive cells in the crystal lattice, and R the lattice vector. Figure 3 shows a correct representation of the exciton energy dispersion that considers its two-particle nature.



Figure 3: Energy states of a Wannier exciton showing bound states (n = 1, 2, 3, solid lines) and the continuum ( $n = \infty$ , dotted line).  $E_g$  is the bandgap and  $E_b$  denotes the exciton binding energy. The dashed line represents the photon dispersion and optical transitions can only occur at intersections with it.

Since the centre of mass motion is translationally invariant, the wave vector conservation required during a photon absorption or emission process only applies to the exciton wave vector, and not to those of the individual electron or hole. Thus, to conserve energy and momentum during the optical transition, the process can only occur at the intersection between the radiation and the exciton dispersion curves, where the photon-exciton interaction couples both entities to form a mixed mechanical-electromagnetic wave, called *exciton-polariton*.

Exploiting the unique properties of this transient species, e.g. for low-threshold lasing [26], involves a research field on its own, which is beyond the scope of this introduction. For the framework of this thesis, we assume an exciton damping term through scattering of excitons e.g. with phonons that is larger than the exciton-photon interaction within the material, thus allowing us to apply Fermi's Golden rule for optical transitions as outlined earlier.

#### 2.1.5 Charge carrier recombination processes

Having understood the electronic structure of semiconductors and the occupation of states by electrons as well as the concept of optical transitions between such energy levels, in this section we will now briefly review the most common charge carrier recombination process responsible for de-excitation. Important coefficients generally observed in the case of metal-halide perovskite semiconductors will be discussed in the next section. These insights into the carrier dynamics form the basis to understand the experimental observations made in Chapters 4 and 5 through time-resolved optical spectroscopy.

We typically consider three major recombination processes that dominate the charge carrier dynamics of excited semiconductors like GaAs or metal-halide perovskites, and which lead to the following rate equation:

$$\frac{dn}{dt} = G - k_1 n - k_2 n^2 - k_3 n^3$$
(23)

Here, the change of carrier density n with time is dependent on a generation rate G, and the recombination constants  $k_1$ ,  $k_2$  and  $k_3$ . This model considers only the existence of free carriers, i.e. the exciton binding energy is low enough that electrons and holes are not bound to each other and can act independently.

We will start with the discussion of the term involving  $k_2$  in this model. It describes the bimolecular radiative recombination of an electron and a hole, which – since it depends on both carrier densities – scales quadratically in n. This two-particle process is equivalent to the description of the radiative band-to-band transition of an excited electron in the conduction band edge as it returns to the valence band edge under emission of a photon. It is thus generally assumed here the electron (n) and hole (p) densities are the same. More generally, the radiative rate would be described as

$$\Gamma_{rad} = k_2 \, (n \, p - n_0 \, p_0) \tag{24}$$

with the background electron and hole densities  $n_0$  and  $p_0$ , respectively – i.e. the amount of charges present in the material in the dark (without photoexcitation or other external stimuli present). As we found in the previous section, the radiative rate is an intrinsic material property related to its band dispersion. Upon (photo-)excitation of the semiconductor, excess carrier populations  $\Delta n$  and  $\Delta p$  of electrons and holes, respectively, will be generated, such that the radiative recombination rate now becomes:

$$\Gamma_{rad} = k_2 \left[ (n_0 + \Delta n)(p_o + \Delta p) - n_0 p_0 \right]$$
  
=  $k_2 \left( \Delta n p_0 + n_0 \Delta p + \Delta n \Delta p \right)$  (25)

Since in most cases the additionally excited carrier population  $\Delta n, p$  will be much larger than the background carrier density, and as stated above we assume equal generation of excited electrons and holes ( $\Delta n = \Delta p = n$ ), we retrieve the initially stated, simpler relation of

$$\Gamma_{rad} \approx k_2 \, n^2 \tag{26}$$

If we instead assumed a purely excitonic population, the radiative rate would become dominated by 'geminate' recombination of electrons and holes. In this correlated case, the radiative rate would then not scale quadratically but linearly with the exciton density  $n_x$ :

$$\Gamma_{rad,X} = k_2 \, n_X \tag{27}$$

We will see this to be the case in the optical experiments carried out on excitonic nanocrystals in Chapter 5.

Similarly, in the case of a strongly doped semiconductor, e.g. n-type, if  $\Delta n$  becomes much smaller than  $n_0$ , radiative recombination will now be dominated by the doping density, such that

$$\Gamma_{rad} \approx k_2 \, n_0 \, \Delta n \tag{28}$$

In a time-resolved experiment, as shown in Chapter 4, the bimolecular recombination will now appear as a monoexponential function of carrier density n, which needs to be distinguished from excitonic recombination, or trap-assisted recombination, considered next.

While in an ideal semiconducting crystal, free of defects, recombination of charges should be purely radiative, in a real semiconductor trap states are present which enable non-radiative recombination of carriers at defect sites. This can occur, if the energy level of the trap lies within the bandgap of the semiconductor, such that electrons or holes can relax into it. Once trapped, the carrier can be de-trapped to re-join the bands – which is energetically unfavoured and thus unlikely – or will recombine with a carrier of opposite charge passing by. Excess energy is mainly released as phonons and thus does not contribute to the radiative performance

of the material. This trap-assisted recombination rate  $\Gamma_{SRH}$  is first order in its kinetics and follows:

$$\Gamma_{SRH} = \frac{n p - n_i^2}{\tau_p (n + n_d) + \tau_n (p + p_d)}$$
(29)

In this model, also called *Shockley-Read-Hall model* [27–29],  $\tau_{n,p}$  represents the lifetime of the electron or hole, respectively, while  $n_d$  and  $p_d$  are the electron and hole densities when their quasi-Fermi level reaches the trap level, respectively, and  $n_i$  the intrinsic carrier density. We can calculate  $n_d$  and  $p_d$ , as they depend on the energy level of the trap  $E_t$  via:

$$n_d = n_i \ e^{E_t - E_{F,i}/k_B T} \tag{30}$$

and

$$p_d = n_i \, e^{-(E_t - E_{F,i})/k_B T} \tag{31}$$

with the intrinsic Fermi level  $E_{F,i}$ . Assuming the trap level is at the same energy position, i.e. in the middle of the bandgap for an undoped semiconductor, and if in a high carrier density regime such that the excited carrier population  $\Delta n = \Delta p = n \gg n_i$ , then it follows:

$$\Gamma_{SRH} \approx k_1 n \tag{32}$$

where

$$k_1 = \frac{1}{\tau_n + \tau_p} \tag{33}$$

Thus, we find a first-order dependence of the recombination rate on carrier density in the case of non-radiative trap-assisted recombination. The solution to the respective differential equation yields for the time-dependent carrier density:

$$n(t) = e^{-k_1 t} \tag{34}$$

As such, in the trap-dominated regime, we expect a monoexponential decay from time-resolved measurements of the carrier density, e.g. observed in transient absorption at low excitation densities.

The third term in the general rate equation (Eq. 23) stated at the beginning of this section, scales cubic in carrier density and thus implies a three-particle collision event. Such a process becomes likely only at very large carrier densities (typically larger than  $10^{17}$  cm<sup>-3</sup>), and the most important mechanism in this regime is that of *Auger recombination*. It involves the interaction of a recombining electron and hole with another electron or hole. Upon recombination of the pair, their excess energy is transferred to a third charge carrier in their vicinity, which is therefore excited into a higher band (or in the most drastic case even ionised,

as exploited in Auger electron spectroscopy). This non-radiative loss channel in the highcarrier density regime, i.e.  $\Delta n = \Delta p = n \gg n_i$ , follows the recombination rate:

$$\Gamma_{Auger} = k_3 n p^2 \tag{35}$$

or

$$\Gamma_{Auger} = k_3 \, n^2 p \tag{36}$$

depending on the recombination partner involved. With  $n \gg n_i$  Auger recombination will outcompete bimolecular (and trap-assisted) recombination at high carrier densities, thus limiting generally the performance of devices at high charge densities, e.g. as one origin of the efficiency droop observed in LEDs.

## 2.2 Semiconductor nanocrystals

Now that we have broadly discussed the relation between electronic structure in bulk solid semiconductors, in this Chapter we take a closer look on the consequences of confinement in nanoscale systems. The general concepts described here will be important to understand the charge carrier dynamics in perovskite nanocrystals studied in Chapter 5.

## 2.2.1 Concept of quantum-confinement in nanocrystals

Let us start with the observations made once a semiconducting material, like for example CdSe, is fabricated on nanometre length scales, such as in a colloidal solution, as shown in Figure 4.



Figure 4: Colloidal solutions containing quantum dots display size-dependent photoluminescence (PL) spectra. Adapted with permission from ref. [30].

Such semiconducting nano-crystallites are often called 'quantum dots' [31,32], referring to the quantum confinement charges in these systems experience and the dot-like quasi-zerodimensionality as compared to materials of longer length scales either in one (e.g. carbon nanotubes), two (e.g. GaAs quantum wells) or three dimensions (i.e. bulk materials). For such nanocrystals we find that the smaller these crystals are synthesised, the higher is the effective optical bandgap of the material and consequently the shorter the wavelength of the light emitted upon photo-excitation.

In order to understand such experimental trends, we first consider the so called 'quantum size effect' which arises when the size of a semiconductor structure becomes comparable to or smaller than the natural length scale of the electron-hole pair, i.e. exciton, that is generated in it. In this case the carriers are confined by the boundaries of the material, giving rise to a quantised electronic structure, as opposed to the bulk band structure of the semiconductor (Figure 5).



Figure 5: Electronic structure of a semiconductor with and without spatial confinement. (a) Band diagram for a two-band model for direct gap semiconductors. (b) Optical transitions in finite size semiconductor nanocrystals, which are discrete due to the quantisation of the bulk bands.

In order to quantify this effect and distinguish between different experimental scenarios, the Bohr radius  $a_B$  of a particle is a useful measure and defined as:

$$a_B = \varepsilon \left(\frac{m_0}{m^*}\right) a_0 \tag{37}$$

with the material's dielectric constant  $\varepsilon$ , the electron rest mass  $m_0$ , the particle's effective mass  $m^*$ , and the hydrogen atom Bohr radius  $a_0$ . Generally, three different limits can be considered, depending on the individual system's dominating optical properties:

- 1. The *strong* confinement regime: If the nanocrystal radius *a* is much smaller than the electron, hole, or exciton Bohr radius, the electron and hole are strongly spatially confined within the material object's boundaries.
- 2. The *weak* confinement regime: When *a* is larger than the individual Bohr radii of the electron and hole, but smaller than that of the exciton, only the exciton's centre of mass motion will be confined.
- 3. The intermediate confinement regime: Here, *a* is in between the electron's and hole's Bohr radius, thus only one type of charge carrier, e.g. the hole, is strongly confined while the other is not.

However, this classification should be seen as a rough guideline rather than a strict rule when trying to relate experimentally determined material properties to their electronic origin – as systems may lie in between these cases.

## 2.2.2 The particle-in-a-sphere model

For a simple and yet rather versatile ansatz that describes experimental optical spectra of a range of nanocrystalline systems surprisingly well, we shall now consider the 'particle-in-a-sphere model'. The model has been successfully employed for the description of nanocrystals in the early pioneering work by Efros [33] and Brus [34], and is presented here in the formalism following Flügge [35] and Messiah [36].

We start with a particle of mass  $m_0$  inside a spherical potential of radius *a*:

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r > a \end{cases}$$
(38)

Then solving the Schrödinger equation for this system yields the wavefunctions:

$$\Phi_{n,l,m}(r,\theta,\phi) = C \frac{j_l(k_{n,l},r) Y_l^m(\theta,\phi)}{r}$$
(39)

where *C* is a normalisation constant,  $j_l(k_{n,l}, r)$  is the spherical Bessel function of order  $l, k_{n,l} = \alpha_{n,l}/a$ , with  $\alpha_{n,l}$  being the *n*<sup>th</sup> zero of  $j_l$ , and  $Y_l^m(\theta, \phi)$  being a spherical harmonic. Possible energy values of the particle are then:

$$E_{n,l} = \frac{\hbar^2 k_{n,l}^2}{2m_0} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_0 \alpha^2}$$
(40)

The eigenfunctions above resemble the atom-like orbitals of the same symmetry and can thus be labelled by similar quantum numbers: n (1, 2, 3 ...), l (s, p, d ...), and m. Consequently, the energies are identical to that of the kinetic energy of a free particle, but quantised by the boundary condition set by the potential well in discrete values of the wavevector  $k_{n,l}$ .

In order to apply this model to semiconductor nanocrystals, we assume bulk isotropic valence (v) and conduction (c) bands that can be described by the 'effective mass approximation'. Following Bloch's theorem, the electron wavefunction in the periodic potential  $u_{nk}$  dictated by the crystal lattice can be expressed as:

$$\Psi_{nk}(\vec{r}) = u_{nk}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$
(41)

with the band index n and wavevector k. The energy of the valence and conduction bands with respect to the bandgap  $E_q$  can then be approximated as:

$$E_k^{\nu} = \frac{-\hbar^2 k^2}{2m_{eff}^{\nu}}$$
(42)

and

$$E_k^c = \frac{\hbar^2 k^2}{2m_{eff}^c} + E_g \tag{43}$$

where the carriers are described as free particles with effective mass  $m_{eff}^{v,c}$ , which is meant to approximate the complicated potential felt by carriers in the lattice, while allowing us to ignore the individual lattice atoms. In order for the bulk-inspired effective mass approximation to hold in a nanocrystal, the nanocrystal diameter has to be much larger than the lattice constant of the material. Within this "envelope function approximation", the single particle (SP) wavefunction can be described as a linear combination of Bloch functions of the form:

$$\Psi_{SP}(\vec{r}) = \sum_{k} C_{nk} \, u_{nk}(\vec{r}) \, e^{i\vec{k}\cdot\vec{r}}$$
(44)

with the expansion coefficient  $C_{nk}$  to ensure that the sum satisfies the boundary condition set by the spherical potential. Assuming a weak dependence of the periodic potential on k, this can be rewritten as:

$$\Psi_{SP}(\vec{r}) = u_{n0}(\vec{r}) f_{SP}(\vec{r})$$
(45)

with the single particle envelope function  $f_{SP}(\vec{r})$ . This decoupling simplifies our initial problem greatly: The periodic potential function can be calculated within the tight-binding model (or linear combination of atomic orbitals, LCAO) as a sum of atomic wavefunctions  $\varphi_n$ via:

$$u_{n0}(\vec{r}) = \sum_{i} C_{ni} \,\varphi_{ni}(\vec{r} - \vec{r}_{i})$$
(46)

As such, what is left is to determine the SP wave function  $f_{SP}(\vec{r})$ , which is the exact problem addressed by the particle-in-a-sphere model above. Therefore, each electron and hole level within the nanocrystal can be described by an atomic orbital that is confined within the nanocrystal, labelled 1*S*, 1*P*, 1*D*, 2*S*, etc. with energy levels as shown above, but with  $m_0$ replaced by the corresponding effective mass.

However, this treatment only accounts so far for a charge in a spherically confined semiconductor, and not the Coulombic attraction between the electron and hole which form an exciton. The importance of this Coulomb term depends on the initially described confinement regime. In the 'strong confinement approximation', this is accounted for as follows: The confinement energy derived above scales as  $1/a^2$  for each carrier, while the Coulomb interaction scales as only 1/a. Thus, the confinement term dominates in the case of very small crystallites so that electron and hole can be treated independently, and the Coulomb term added

as a first-order correction  $E_c$  in a subsequent step. The exciton states can therefore be expressed as [37]:

$$\Psi_{Ex}(\vec{r}_{e},\vec{r}_{h}) = \Psi_{e}(\vec{r}_{e}) \Psi_{h}(\vec{r}_{h}) = u_{v} f_{h}(\vec{r}_{h}) u_{c} f_{e}(\vec{r}_{e})$$
$$= C \left[ u_{v} \frac{j_{L_{h}}(k_{n_{h},L_{h}} r_{h}) Y_{L_{h}}^{m_{h}}}{r_{h}} \right] \left[ u_{c} \frac{j_{L_{e}}(k_{n_{e},L_{e}} r_{e}) Y_{L_{e}}^{m_{e}}}{r_{e}} \right]$$
(47)

and have the corresponding energy values:

$$E_{Ex}(n_h L_h n_e L_e) = E_g + \frac{\hbar^2}{2a^2} \left( \frac{\alpha_{n_h, L_h}^2}{m_{eff}^v} + \frac{\alpha_{n_e, L_e}^2}{m_{eff}^c} \right) - E_C$$
(48)

Here, for example the lowest pair state would be labelled as  $1S_h 1S_e$ , and the first-order Coulomb term accordingly be  $1.8e^2/\epsilon a$ .

## 2.2.3 Refined models

In order to account for a more realistic band structure than the simple parabolic bands approximated above, more complicated models are necessary. For example, the valence band in CdSe arising from the Se 4*p* atomic orbitals leads to a six-fold degenerate band at k = 0, including spin [38]. Here, strong spin-orbit coupling lifts this degeneracy and creates sub-bands with the total angular momentum *J* ranging from -3/2 to +3/2, as shown in Figure 6.

A more accurate approach is presented by the  $k \cdot p$  method, where the bulk bands are expanded analytically around a particular point in k space. Around this point, often k = 0, the band wave functions and energies can be solved precisely, and then extended within perturbation theory of sufficient order to deliver satisfactory results. A detailed discussion can be found e.g. in the book by Kittel [39].

A suitable treatment of the beforementioned problem of the six-fold degenerate valence band found in semiconductors with diamond-like structure is presented by the Luttinger Hamiltonian [40], a 6 by 6 matrix derived within the degenerate  $k \cdot p$  perturbation theory. However, this '6-band model' does e.g. not include the crystal field splitting present in wurtzite lattices and is thus again limited in its application.



Figure 6: Valence band structure of semiconductors with different crystal structure. (a) In a diamond-like semiconductor, spin-orbit coupling splits the valence band into two bands of different total angular momentum J, the lower one is often called split-off (so, or C) band. The upper band is split further as it diverges from k = 0, forming the heavy-hole (*hh* or A) and light-hole (lh or B) sub-bands of different projections of  $J_m$ . (b) In a wurtzite structure, the crystal field of the hexagonal lattice splits the A and B bands also at k = 0.

To also include coupling between valence and conduction bands, significant for example in narrow-gap semiconductors, the Kane model [41,42] became the approach of choice widely used in nanocrystal studies. Here, a small subset of bands containing the bands of interest are treated exactly, while the outlying bands are included within the second-order  $k \cdot p$  method. Hence, the dispersion of each band is no longer strictly parabolic and often describes experimental data to a larger extent.

As a final remark, it should be noted that this chapter was only meant to give a brief overview of generals approaches to treat the complicated electronic system present in nanocrystals. An impressive example of a state-of-the-art application of the Kane model to the electronic structure in the special case of pseudo-cubic perovskite nanocrystals was recently shown by Efros and others in ref. [43]. It also presents a detailed derivation for the case of cubic rather than spherical nanocrystals and models their complicated interaction with light propagating through this anisotropic environment., which is beyond the scope of this chapter.

Their proposed energy level diagram for the perovskite nanocrystals is shown in Figure 7.



Figure 7: Bright triplets in perovskite nanocrystals. The crystal structure of pseudo-cubic CsPbBr<sub>3</sub> perovskite shows inversion asymmetry (here: along the z direction) and hence the resulting Rashba effect splits the energy states in such a way that the lowest-lying energy state is an optically active triplet. Illustration based on ref. [43].

The study showed that the lowest exciton in caesium lead-halide perovskites involves a highly emissive state arising from a combination of strong spin-orbit coupling (SOC) in the conduction band and the Rashba effect [44]. The latter states that in semiconductors with strong spin-orbit coupling and inversion asymmetry, the spin-dependent fine structure changes and depending on the direction of asymmetry, such that the sub-bands split by the total angular momentum quantum numbers projected in the z direction will have lower or higher energies than without this inversion asymmetry. Reasons discussed in the literature for the inversion-symmetry breaking found in the perovskite nanocrystals include cation positional instabilities [45] or surface effects [46], but are still part of an active field of research at this point.

# 2.3 Device applications of semiconductors: Solar cells and lighting

One of the long-term objectives that motivate the work performed in this thesis is to identify promising semiconductors and their underlying charge dynamics in order to employ them in useful and efficient devices in the future. The most important optoelectronic application currently under research for perovskite materials is photovoltaics, followed by light-emitting devices, and I will thus briefly outline the underlying device physics in this chapter.

#### 2.3.1 Solar cells

A solar cell is a device which exploits the photovoltaic effect in order to convert light energy, e.g. emitted by the sun, to electric energy. This effect was first demonstrated in 1839 by Bequerel [47], but it took until 1954 for the first useful solar cell based on a silicon p-n junction to be developed by Chapin et al. at Bell Labs [48].

While most commercially available solar cells are still fabricated from crystalline silicon to date, besides other thin film technologies like CIGS, it is mostly organic photovoltaics (OPV) and solar cells based on perovskite semiconductors which hold great promise for the next generation of photovoltaic devices with high cost-effectiveness, combined with versatile integration, e.g. in flexible devices. For comparison: The highest efficiency reported by the National Renewable Energy Laboratory for single-crystalline (non-concentrator) silicon is 26.1%, while that of OPV is 17.4% and that of a perovskite solar cell is 25.2% – and even higher for tandem devices (ref. [49], accessed on 1<sup>st</sup> September 2020).

The high performance of perovskite-based cells appears even more impressive given that research on this material class began only in 2009, when Tsutomu Miyasaka and colleagues pioneered the use of hybrid halide perovskites in photovoltaics [50].

For the most common solar cell architecture, we consider doped semiconductors. In a negatively doped, n-type semiconductor, impurities with higher valency than the bulk material are incorporate. An example is the doping of silicon (4 valence electrons) with phosphorus (5 valence electrons). The additional electron of the donor is readily released into the conduction band of the host material – if weakly enough bound: at room temperature – thus raising the Fermi level. Conversely, for positive p-type doping an atom of lower valency than the host material is employed to substitute a small amount of its atoms, e.g. boron (3 valence electrons) for silicon. The additional holes, or reduction of electrons previously available in the valence band and now bound to the electropositive impurity, will conversely push the Fermi level closer to the valence band.

Next, we consider the flow of charges when a negatively doped n-type semiconductor is brought into contact with a positively doped p-type semiconductor, as illustrated in Figure 8.

#### **Chapter 2: Theoretical Background**



Figure 8: The p-n junction. The band diagram shows n- and p-type semiconductors with their respective Fermi level positions (top). Once brought into contact (bottom), charges flow until the diffusion of carriers leads to an equilibrium concentration across both materials with a shared Fermi level.

We find that at this p-n junction, electrons and holes flow until they have reached an equilibrium, i.e. the resulting electric field has brought the net current to zero, and the Fermilevels of both materials are aligned. While electrons diffuse from the n-doped to the p-doped side and holes vice versa, they will predominantly recombine at the junction with their countercharge. This will leave the charged dopant ions at each side behind, causing a voltage build-up across the junction, that lets carriers drift and will eventually balance out carrier diffusion until the net current flow is brought to zero. The resulting area of low carrier density at the junction is called the 'depletion zone', or space-charge region due to the presence of the ions.

The resulting built-in potential  $V_b$  across the junction depends on the doping concentration of donated electrons  $N_n$  and donated holes  $N_p$  of both materials, as well as the intrinsic carrier density  $n_i$  via:

$$V_b = \frac{k_B T}{q} \ln\left(\frac{N_n N_p}{n_i^2}\right) \tag{49}$$

This device asymmetry is important to create an external voltage which allows electrons and holes to be directed into different layers and thus separated from each other. Once a photon is absorbed e.g. in the p-type layer, the generated electron and hole will diffuse in this layer. If they reach the depletion zone, the electron will drift to the n-type layer since the latter will be lower in energy level, whilst the hole will remain confined to the p-type layer, since it cannot cross the built-in potential barrier. The opposite scenario is the case for the absorption of a

photon in the n-type layer. Once transferred to the electrodes at both sides of the device, the electronic circuit is complete and useful electric energy can be extracted.

Thus, it is apparent that in order for this process to be efficient, long charge carrier lifetimes and high mobilities are favourable which lead to long diffusion lengths (with respect to the absorption depth) that increase the chance of carriers to reach the respective electrode layer. Here, the carrier diffusion length  $l_D$  is connected to diffusion constant D and the carrier lifetime  $\tau$  via:

$$l_{\rm D} = \sqrt{D\tau} \tag{50}$$

The diffusion constant is related to the material-specific carrier mobility  $\mu$  via the *Einstein-Smoluchowski relation* [51,52] for diffusion of charged particles as follows:

$$D = \frac{k_B T \mu}{q} \tag{51}$$

Besides high mobilities, from a material perspective ohmic contacts are desirable for efficient carrier extraction, while the semiconductor itself should have a high radiative bimolecular recombination constant and high absorption. We shall later see that perovskites perform remarkably well in all these key parameters, given their simple and crude fabrication from solution.

Yet, because controlled chemical doping of perovskite materials is still problematic to date, for these semiconductors mostly another solar cell architecture is employed: the *double heterojunction*, shown in Figure 9.



Figure 9: Idealised double-heterojunction with an electron transport layer (ETL) and a hole transport layer (HTL) on both sides of an intrinsic semiconductor (e.g. perovskite) to facilitate separation of electrons and holes.

Here, a heterojunction simply describes the interface between two semiconductors with different bandgaps (as opposed to a homojunction). In the case of a double heterojunction, an intrinsic absorber, e.g. perovskite, is sandwiched between two layers of high-bandgap semiconductors. These two layers act as hole- and electron-selective transport layers through the choice of the band alignment. Together, the three layers form a p-i-n junction. While for a readily dopable semiconductor like silicon these three layers could simply be formed from p-, n-, and undoped Si, for perovskites often more chemically diverse materials are employed. Examples are TiO<sub>2</sub> or ZnO as electron accepting layer and 2,2',7,7'-tetrakis[N,N-di(4-methoxy-phenyl)amino]-9,9'-spirobifluorene (spiroOMeTAD) or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as hole accepting layer. Note that in the sketch shown the energy levels of the extraction layers are perfectly aligned, while in reality band bending near the junctions will occur at slight misalignment, causing electric fields that can be either beneficial or harmful to charge transport.

Now that we have understood the general energy landscape set out in conventional solar cells, let us next discuss the parameters relevant to device performance whose optimisation is a long-term goal of the work carried out within this thesis. The formulae in the following are based on the excellent overview given in the book by Nelson [53].

When mentioning the solar cell efficiency, we usually refer to the 'power conversion efficiency' (PCE)  $\eta$ , which is defined as the ratio of electric power  $P_{elec}$  extracted to the light power  $P_{light}$  incident on it:

$$\eta = \frac{P_{elec}}{P_{light}} \tag{52}$$

As such, the PCE accounts for all losses, both internal ones like non-radiative recombination at trap sites within the material, but also external ones like external reflection of light that is not coupled in due to a high refractive index mismatch. To quantify the efficiency of a solar cell, typically a solar simulator is used to reproducibly emulate the sun light in a given atmosphere and of given spectrum and intensity. Then, the current-voltage characteristic of the device is measured, without and with the light source present. In the dark, the *J-V* curve shows the standard diode characteristic with the dark current  $J_{dark}$  following:

$$J_{dark} = J_0 \left( e^{qV/k_B T} - 1 \right)$$
 (53)

Figure 10 illustrates this relation, and also the following concepts and definitions.



Figure 10: Typical current-voltage (*J-V*) characteristic of a solar cell in the dark (black line) and under illumination (orange line). Some special points mentioned in the text are indicated.

Under illumination, this diode curve is then shifted along the current axis such that a current flows, even if a small opposite voltage bias is applied. It is a convention to assign the photocurrent a positive value and thus the overall current  $J_{illu}$  has the form:

$$J_{illu} = J_{SC} - J_0 \left( e^{qV/k_B T} - 1 \right)$$
(54)

Here,  $J_{SC}$  describes the current measured under short-circuit condition, where no bias is applied to the device and electrons can hence move freely like in a shorted circuit. In an idealised device, this current would equal the photon flux incident.

As a second key parameter, the external bias is being increased to the extent where the current stops flowing entirely. This yields the open-circuit voltage  $V_{OC}$ . Here the bias balances the voltage caused by the photovoltaic effect. Setting the current in the above equation to zero derives this parameter as:

$$V_{OC} = \frac{k_B T}{q} \ln\left(\frac{I_{SC}}{I_0} + 1\right)$$
(55)

While in principle the device could be operated at any point on the *J*-*V* curve, in order to extract the maximum amount of power, we should choose the maximum power point  $P_m$  where the current and voltage are maximised according to:

$$P_m = J_m V_m \tag{56}$$

In an ideal cell, the *J*-*V* curve would be rectangular, and the special coordinates above would be identical to the product  $J_{SC}V_{OC}$ . The performance of the device is therefore often quantified by the so called 'fill-factor' *FF* which describes the deviation from the ideal value via:

$$FF = \frac{P_m}{J_{SC}V_{OC}}$$
(57)

Rearranging this leads to an expression for the PCE outlined above as:

$$\eta = FF \frac{J_{SC} V_{OC}}{P_{light}}$$
(58)

Since a non-ideal solar cell will have a contribution of non-radiative recombination to the total recombination rate of charge carriers in the system, it is useful to quantify this performancelimiting property directly from the measured *J*-*V* curve of said device. Ross demonstrated in 1967 [54] that the  $V_{OC}$  is a probe for the non-radiative recombination as it decreases with increasing losses. This may appear counter-intuitive, given that the overall short-circuit current should be reduced through the higher total recombination rate and charges won't be able to contribute to the measured current anymore. However, under operating conditions, the extraction of carriers will be faster than their recombination, such that the impact of non-radiative losses on the  $J_{SC}$  becomes negligible. Under  $V_{OC}$  conditions, carriers will however not be extracted and will thus recombine eventually, depending on the losses present in the cell. As such, the device parameter  $V_{OC}$  is directly related to the ratio of radiative to total recombination rates stated by the external photoluminescence quantum efficiency (PLQE) via:

$$qV_{OC} = qV_{ideal} - \frac{k_B T}{q} \ln(PLQE)$$
(59)

The PLQE is the figure of merit that I will mostly be concerned within the spectroscopic framework of this thesis, but it is apparent that this will also directly impact device performance and should therefore be maximised. The same holds true for operating a device towards maximised electroluminescence quantum efficiency (EQE) in a light-emitting diode – or to state this more explicitly: "A great solar cell also needs to be a great light-emitting diode" [55]. If the PLQE is large, strong photon-recycling can occur, usually observed under open-circuit condition. This has also been reported in perovskites [56,57] and requires, aside from the high radiative fraction of carrier decay, generally a high spectral overlap between absorption and emission for the re-absorption to occur efficiently, facilitated by a high refractive index of the semiconductor compared to its surrounding. This will cause a narrow light escape cone and thus stronger re-absorption of the internally reflected photons forming the internal luminescence photon gas. However, even without photon recycling as a dominant process, the  $V_{oc}$  and thus solar cell efficiency will still increase with the PLQE as shown by the above equation and also modelled recently by Bowman et al. [58].

## 2.3.2 Light-emitting devices

In a light-emitting device (LED), or more specifically here diode, the energy landscape set out by the heterojunctions described in the previous section can in principle be employed as well. The concept of operation is reversed, changing from a "photons in, electricity out" principle in a solar cell to an "electricity in, photons out" direction for an LED. Such electroluminescent devices employ to date – similar to their solar cell analogues – mostly inorganic III-V semiconductors like GaAs, or silicon. However, in tandem with the developments over the last decades in solar cell technologies, so too do new material platforms emerge in the lighting research field. Famous examples are LEDs based on semiconducting polymers [59,60] or small phosphorescent molecules [61,62] – leading to organic LEDs (OLEDs), those based on colloidal nanocrystals [63], or most recently based on perovskites as light-emitting material [64]. The latter have achieved lately record-efficiencies beyond 12% EQE in the blue [65], a spectral region where high efficiencies are particularly hard to achieve in.

Figure 11 shows a typical LED architecture consisting of an intrinsic active layer in a doubleheterojunction structure, with an n-type electron transport layer (ETL) and a p-type hole transport layer (HTL). Typical ETLs employed in LEDs are  $TiO_2$  or the fullerene-based phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM), while typical HTLs are PEDOT:PSS or poly(9,9'-dioctylfluorene) (F8).



Figure 11: LED band alignment, employing a double-heterojunction with an electron transport layer (ETL) and a hole transport layer (HTL) on both sides of an intrinsic semiconductor (e.g. perovskite) to facilitate injection of electrons and holes and their subsequent recombination in the emissive layer.

In operation, i.e. under forward bias, electrons and holes are then injected from the cathode and anode, respectively. The band alignment of the following ETLs and HTLs is ideally chosen

such, that charges are directed to a thin active layer, where they recombine radiatively, emitting light in all directions.

In the case of typical bulk perovskites, as we shall discuss in the next section in more detail, the inherently low exciton binding energies which facilitate charge separation in solar cells, are undesirable in an LED. Thus, to promote radiative recombination, the active region should be fabricated as thin as possible, to confine carriers spatially. Other strategies to achieve this are based on layered perovskites or nanocrystals, where more stable excitons are readily formed.

## 2.4 Metal-halide perovskites

This section will introduce the material class of metal-halide perovskites, which were the main focus of the studies during my PhD work. We will start with an introduction of the general structure and chemical composition found for these semiconductors, and then discuss their electronic structure and related charge carrier dynamics.

## 2.4.1 Structure and chemical diversity of metal-halide perovskites

The materials investigated in this thesis in both bulk and nanocrystalline form are based on an emerging class of semiconductors called *metal-halide perovskites*. The name is based on the perovskite crystal structure whose word was coined to name the mineral CaTiO<sub>3</sub>, which adapts this specific structure. The mineral was discovered in the Ural Mountains by the German mineralogist Gustav Rose in 1839, and named in honour of the Russian Count, Lev. A. Perovski [66]. Since then, many materials adapting this ABX<sub>3</sub> structure were found and they all have in common the A- and B-site cations of different sizes, as well as an anion X coordinating B, as shown in Figure 12.



Figure 12: Perovskite crystal structure following the general formula ABX<sub>3</sub>, where BX<sub>6</sub> octahedra coordinate around a central A-site cation in a cubic fashion. Typical ions used in modern metal-halide perovskite semiconductors are shown (MA: methylammonium, FA: formamidinium).

The A-site cations are usually larger than the B-site cations, and the B-site cation is sixcoordinated by the X-site anion to form a  $BX_6$  octahedron. Those octahedra are corner-shared to form a 3D framework, in which A-site cations are located in the framework cavities.

The metal-halide perovskites studied in this thesis for their unique optoelectronic properties form a sub-class, where the A-site typically is a cesium or organic amine monocation – hence the term 'hybrid organic-inorganic' is often encountered. B describes the lead dication and X is a halide anion. The organic components are assumed to introduce structural flexibility not accessible by their purely inorganic counterparts [67], though often at the cost of lower stability, while Cs-based perovskites have demonstrated high performance in optoelectronic applications as well.

The prototypical metal-halide perovskites studied mostly in their semiconductor context currently were first structurally characterised by Weber in 1978 [68], reporting the cubic phases of MAPbX<sub>3</sub> (MA: methylammonium, X: Cl, Br, I).

It then took until the year 2009, when Tsutomu Miyasaka and colleagues first employed such hybrid metal-halide perovskites in a solar cell [50], which remains their premier device application investigated to date.

Since then, many different A-site cations have been explored, benefitting from the abundant variations of organic components and metal salts available. In order to form stable crystal structures, however, the ratio of ionic radii of the building blocks employed is important. The

Goldschmidt tolerance factor (t) is a useful parameter to predict if the perovskite architecture can tolerate a certain ion [69]. A selection of the most studied ions is shown in Figure 13.



Figure 13: Tolerance factor for a variety of A-site cations and their suitability to form a stable perovskite crystal structure; Values taken from ref. [70]. MA, FA, IA, EA and Gua abbreviate methylammonium, formamidinium, imidazolium, ethylammonium, and guanidinium ions, respectively.

Because the A- and/or X-site ions are replaced by molecular structures, the tolerance factor is adapted in the following way:

$$t = \frac{r_{A_{eff}} + r_{X_{eff}}}{\sqrt{2}(r_B + h_{X_{eff}}/2)}$$
(60)

where  $r_B$  denotes the Shannon ionic radius of the B-site metal ion,  $r_{A_{eff}}$  the effective radius of the A-site cation, and  $r_{X_{eff}}$  and  $h_{X_{eff}}$  the effective radius and length of the X-site ion, respectively. It was found empirically that combinations of ions lying in the range of ~0.8 – 1.0 form stable compounds [71].

This structural diversity goes hand in hand with the rich electronic properties of metal-halide perovskites. By varying the halide ratio and cations, the bandgap can be readily tuned throughout the visible spectrum, as shown in Figure 14.



Figure 14: Tunability of the bandgap through chemical composition in metal-halide perovskites. (a) Varying the halide ratio of the prototype composition MAPbX<sub>3</sub> has been shown to cover the entire visible spectrum, from 390 to 790 nm. Reproduced with permission from ref. [72]. (b) Extending the compositional space to different A- and B-site cations for further tailoring of the ionisation energy and electron affinity values (derived from photoemission studies), as well as the optical gaps. Reproduced with permission from ref. [73].

While especially the halide ratio-induced bandgap tuning was extensively studied in the past, it should be noted here that the miscibility of halides forming stable compositions is not continuous throughout a phase diagram. Beyond a certain threshold of halide-ratio (e.g. Br/I), phase separation into phases that are richer or poorer in one or the other halide occurs. These additional phases require extra care when handling mixed-halide compositions, given that the pure-halide analogues undergo temperature-dependent phase transitions themselves, as they transform from a cubic to a tetragonal to an orthorhombic phase with lower temperature. Figure 15 gives an overview of these phases as derived from X-ray diffraction experiments.

(a)



Figure 15: Phase diagram of MAPb( $I_{1-x}Br_x$ )<sub>3</sub> solid solutions, as derived from synchrotron-based X-ray diffraction. Reproduced with permission from ref. [74].

Notably, Hoke et al. observed that phase-separation can be driven by illumination of such mixed-halide lead perovskite alloys, and that this effect is partially reversible in the dark [75]. The 'Hoke-effect' termed phenomenon can not only be tracked readily in absorption or photoluminescence measurements, where new spectral features of iodide- and bromide rich phases occur, and the mixed-phase peak is reduced in intensity. It also plays also a role in the current-voltage hysteresis observed in devices [76] due to ion migration [77] and can thus be performance-limiting.

We shall see, however, in Chapter 4 that phase-segregated perovskite materials do not have to mitigate performance *per se*, as their modulated energy landscape can assist carrier funnelling for higher recombination efficiencies.

## 2.4.2 Electronic structure of metal-halide perovskites

Metal-halide perovskites, especially those based on the MAPbX<sub>3</sub> prototype, have demonstrated remarkable optoelectronic properties, including large absorption coefficients, long carrier

diffusion lengths exceeding 1  $\mu$ m [78], low exciton-binding energies, high carrier mobilities, low non-radiative minority-carrier recombination rates, high photoluminescence quantum yields, long carrier lifetimes, high open-circuit voltages in devices, and only shallow defects in the bandgap [79]. Their performance appears even more impressive, given their straightforward synthesis and low-temperature solution-processability.

The existence of only shallow defects and the disperse valence band are both related to the underlying electronic structure, which we shall discuss next. Figure 16 shows a typical orbital diagram of MAPbI<sub>3</sub> as it originates from a tight-binding approach, or linear combination of atomic orbitals (LCAO), as well as the associated computed density of states.



Figure 16: Orbital diagram of MAPbI<sub>3</sub>, where the atomic lead and iodine orbitals form bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) molecular orbitals, which form the energy bands in the semiconductor lattice. (b) Projected density of states for the different species involved in band formation computed using DFT including spin-orbit interactions. Adapted with permission from ref. [80]. Note that the MA<sup>+</sup>, or generally the A-site cation is not electronically active, according to the current understanding in the literature [81].

The presence of filled Pb 6*s* orbitals, deriving from the partial oxidation of Pb relative to its Pb<sup>4+</sup> oxidation state, explains both the shallow binding energy of defects and the atypical dependence of the bandgap on strain or temperature. The band structure of having bonding orbitals at the conduction band minimum (CBM) and anti-bonding orbitals at the valence band maximum (VBM) is markedly different than that in most semiconductors (e.g. III-V ones), where the valence band is composed predominantly of bonding states and the conduction band consists of wavefunctions with dominant anti-bonding character [80].

If the orbitals are instead anti-bonding at the VBM and bonding at the CBM, any dangling, i.e. broken bonds forming upon creating a vacancy will likely appear as resonance *inside* the bands, rather than within the bandgap – thus keeping the latter free of deep states that could act as carrier traps. Similar arguments also are valid for other types of defects like interstitials or antisites, and structural defects like grain boundaries, which consist of many strained and/or dangling bonds. Only extrinsic impurities should therefore introduce deep traps within the bandgap, depending on their energy levels. There are mainly three contributions to the valence band in MAPbI<sub>3</sub>:

- 1. The overlap of the Pb 6s and I 5p orbitals leads to the deeper part of the valence band, which is predominantly of I 5p character, and also to the bottom part of the conduction band, mostly composed of Pb 6s atomic orbitals. Thus, these interactions are responsible for forming the chemical bonds as a result from charge transfer from the Pb 6s to the I 5p orbitals.
- 2. The Pb 6s-I 5p interactions lead to the creation of two bands; a deeper bonding valence band, and the antibonding maximum of the valence band. Therefore, changing the halide ion to tune the bandgap of the material, mostly implies changing the valence band edge, while the conduction band edge remains almost invariant.
- 3. Since only one of the I 5*p* orbitals is oriented along the Pb-I bond, only one out of three of these orbitals are strongly interacting with the Pb 6*s* and 6*p* orbitals. The other two I 5*p* orbitals are oriented orthogonally and can hence only interact with other I 5*p* orbitals, forming the middle of the valence band.

Hence, the bonding-type defect-tolerance arguments can only hold for defects that would tend to create valence band-derived states, like cation vacancies. In contrast, if halide vacancies form, the resulting dangling bonds will appear as resonances inside the conduction band only if the dispersion and bandwidth of the latter are such that the CBM falls below the energy of the Pb 6*p* orbitals. For lead (in contrast to e.g. Ge and to a high extent Sn), this condition is likely due to relativistic spin-orbit interactions that increase the width of the Pb 6*p* conduction band by ca. 2 eV according to calculations [82]. Therefore, the fact that vacancy defects are resonant in the bands is a result of (i) the presence of anti-bonding orbitals within the valence band pushing the VBM energy upwards, and (ii) relativistic effects pushing the CBM energy downwards.

### 2.4.3 Charge carrier dynamics of metal-halide perovskites

With a general picture of the electronic structure in perovskites in mind, we next briefly discuss the charge carrier recombination processes dominant in these systems. Figure 17 gives a brief overview of the most important photophysical processes.



Figure 17: Photophysical processes and charge carrier recombination rate constants of MAPbI<sub>3</sub>, shown for a range of excitation carrier densities  $n_0$ . Reproduced with permission from [83].

For bulk (3D) perovskites, small exciton binding energies on the order of 2-20 meV (for MAPbI<sub>3</sub>, higher for other halides) have been reported [84–87], indicating mainly free charges are present in the material at room temperature. As such, a general rate equation of charge carrier recombination [79,88] has been proven useful to describe experimentally measured carrier dynamics, often determined through photo-induced terahertz conductivity or time-resolved photoluminescence and transient absorption methods, as shown in the upcoming chapters. As discussed in the previous sections, such a differential equation can have the form:

$$-\frac{d n(t)}{dt} = -G(t) + k_1 n(t) + k_2 n^2(t) + k_3 n^3(t)$$
(61)

Here, *n* describes the carrier density, *G* is the charge generation rate (e.g. determined by the photon flux when light with a CW laser is constantly shone on a sample), and  $k_1$ ,  $k_2$ , and  $k_3$  are recombination constants. Typically, for perovskites  $k_1$  is assigned to first-order trap-

assisted recombination,  $k_2$  describes bimolecular radiative recombination of electrons and holes, and  $k_3$  quantifies trimolecular Auger loss mechanisms at higher charge densities. Such multi-particle recombination begins to dominate the excited state-lifetime at carrier densities ca.  $>10^{17}$  cm<sup>-3</sup>, while trap-assisted first-order processes form the major excitation decay response at low carrier densities, of approx.  $<10^{14}$  cm<sup>-3</sup>, depending on the trap density present in the specific perovskite material made. Since solar cells usually operate at around 1 sun, which is equivalent to about  $10^{15}$  cm<sup>-3</sup> for the solar spectrum, they often are dominated by firstorder processes. Therefore, the goal is generally to achieve the lowest possible trap densities (or  $k_1$  constants), and thus long carrier lifetimes at low carrier densities for high-performing devices.  $k_1$  values >10 µs<sup>-1</sup> are readily available with perovskites [89], strongly dependent on the material fabrication process and crystalline quality. In contrast, in a direct bandgap semiconductor, the bimolecular recombination constant is thought to be an *intrinsic* material property, and its coefficient typically resides on the order of 10<sup>-10</sup> cm<sup>-3</sup> s<sup>-1</sup> at room temperature, depending on the experiment [88-90]. Interestingly, the average Auger recombination coefficient in perovskites was reported to be ca. 10<sup>-28</sup> cm<sup>6</sup> s<sup>-1</sup> [79], which is about 25 times higher than that for GaAs [91], implying perovskite materials are less suitable to be employed in high-carrier density applications.

Considering the dynamic changes observable in the optical spectrum of perovskites, strong band-filling effects and bandgap renormalisation have been observed at high excitation densities in ultrafast TA experiments [92], where a carrier-density-dependent blue-shift and broadening of the photo-generated ground-state bleach can be seen. This indicates charge carrier accumulation and is explained on the basis of the (dynamic) Burstein-Moss effect. The band edge states lead to higher-energy optical transitions as a consequence of the Pauli exclusion principle. Furthermore, hot carrier cooling was observed from ultrafast TA experiments, which has been shown to slow down considerably at high carrier densities above a critical injection density of about  $5 \times 10^{17}$  cm<sup>-3</sup>, attributed to a hot-phonon bottleneck [93,94].

## 2.4.4 Perovskite-related materials of reduced dimensionality

So far we have only considered the structure and properties of so called '3-dimensional' bulk perovskite materials, where the structural motif displayed in Figure 12 is translated in all three spatial dimensions to form the crystal lattice of the semiconductor. However, in the quest for new and potentially even higher performing materials, structurally related materials have been investigated as well, some of which are based on reducing the dimensionality of the photo-active material, discussed in this section.

A class of such related materials are the so-called '2-dimensional perovskites' (see e.g. refs. [95–97], and references therein) which are conceptually derived from the parent perovskite structure by isolating a given number of metal-halide octahedra using long organic spacer ligands (Figure 18).



Figure 18: Illustration of the concept of low-dimensional perovskites (n = 1, 2, ...) and how they are structurally derived from the parent bulk perovskite ( $n = \infty$ ). Here, the (100) oriented Ruddlesden-Popper family of the type (RNH<sub>3</sub>)<sub>2</sub>A<sub>n-1</sub>B<sub>n</sub>X<sub>3n+1</sub> (R is an organic rest) is shown (axis oriented vertically).

As the perovskite structure is 'cut' into layers, the size limitation with respect to the tolerance factor seen in the bulk perovskites are less strict and can be widely engineered, together with the optoelectronic properties. Often, long-chain alkyl ammonium ligands are used as spacer ligand, which – owing to their much lower dielectric constant – results in an electronic isolation between given semiconducting  $B_2X_7^{3-}$  layers. As a result, these materials behave like natural self-assembled quantum-well structures with high exciton binding energies (>100 meV) dictated by the confinement between layers, which are readily tuned through the chemical composition and connected layer numbers. Note that the above figure only illustrates the Ruddlesden-Popper material family, whereas other phases like the Aurivilius or Dion-Jacobson layered structures would have a different stacking behaviour and feature e.g. dicationic ligands instead [98]. Furthermore, often not all desired representative structures of increasing layer thickness can be crystallographically evidenced and instead mixed-phase compounds are fabricated.

Not only can the confinement enhance photoluminescence yields in general, but mixeddimensional layered compounds formed through mixture of cations of different sizes can also be used to observe energy funnelling from higher to lower bandgap areas across the material. Thus, two-dimensional perovskites have attracted considerable attention not for use in solar cells [99], but even more so in the context of light-emitting applications [100,101].

In contrast, one-dimensional polymorphs of APbX<sub>3</sub> compounds (like 1D-hexagonal or 1Dorthorhombic phases) are not appealing semiconductors because of their much larger bandgaps and poor electronic transport [102].

In the extreme limit, considering not layers, but individual and separated metal-halide octahedra can be considered a zero-dimensional analogue of (structurally distorted) perovskites. As an example, Cs<sub>4</sub>PbBr<sub>6</sub> and shows high PLQEs of 45% [103], as compared to its 3D counterpart CsPbBr<sub>3</sub> with more than 100 times lower yields. The Karunadasa Group also reported N1-methylethane-1,2-diammonium lead bromide [104], where the high degree of possible octahedral distortion results in white-light emission, assigned to the existence of self-trapped excitons which were also reported for certain 2D-layered perovskites.

These structurally '0D' perovskite materials should be distinguished from perovskite nanocrystals. Those exhibit spatial confinement through their colloidal growth on the nano-scale, but consist otherwise of the 3D bulk semiconductor materials discussed earlier. Because I study such perovskite 'quantum dots' in Chapter 5 of this thesis, we shall briefly discuss the general properties of these nano-engineered materials in the following.

## 2.4.5 Metal-halide perovskite nanocrystals

Semiconducting nanocrystals (NCs) based on metal-halide perovskites were pioneered by Kovalenko and co-workers [105] who demonstrated excellent optical properties of colloidally-synthesised all-inorganic cesium lead halide NCs, as shown in Figure 19.



Figure 19: Colloidal CsPbX<sub>3</sub> perovskite nanocrystals. (a) Solutions of varying halide composition in toluene under UV lamp ( $\lambda = 365$  nm). (b) Normalised photoluminescence spectra. (b,c) Transmission electron microscopy (TEM) images of CsPbBr<sub>3</sub> NCs with average size of 8 nm and scale bar as indicated. Adapted with permission from ref. [105].

The colloidal synthesis of freely suspended crystallites is a surfactant-controlled coprecipitation of the ionic precursor salts that proceeds with fast reaction kinetics even at roomtemperature. Similar to their bulk counterparts, the bandgap can be readily tuned across the visible spectrum through the chosen halide ratio. Moreover, the nanocrystals display sharp absorption and emission spectra of down to 12 nm full width at half maximum (FWHM) in the blue limit with only small Stokes shifts, as in conventional (e.g. CdSe) quantum dots. In contrast to bulk perovskite materials, in nanocrystals the spatial confinement leads to large exciton binding energies (e.g. 75 meV for CsPbCl<sub>3</sub> NCs of ~10 nm size [105]) and thus the effective bandgap of the material can be further tuned through the NC size via the employed reaction times and quenching [102]. Owing to their electronic structure as a perovskite semiconductor outlined above, these nanocrystals are also inherently defect-prone and trapstates tend to form only within the bands, rather than within the bandgap. Together with the fast, few ns short excitonic radiative recombination rate in the confined quantum dots, this leads to extremely high PLQEs near unity.

The combination of high PL yields and highly saturated colours from their narrow emission bandwidths make perovskite NCs promising materials for wide-colour-gamut displays and lighting with a high colour-rendering index, with up to 100% of the International Telecommunication Union Rec. 2020 standard, or even 140% of the older NTSC colour standard [105]. The recent report of coherent single-photon emission from perovskite NCs makes these materials also promising for quantum information processing [106].

Furthermore, the doping of perovskite nanocrystals has been reported, mostly with transitionmetal ions like nickel or manganese, which led to significantly increased PLQEs approaching unity [107–109]. Therefore, doping is considered a promising route towards maximising efficiencies in perovskite-based light-emitting applications [110,111]. However, to date there is no clear mechanism explaining why the excitonic photoluminescence yield is enhanced through doping, aside from potential passivation of traps.

In Chapter 5 of this thesis I will show that beyond the reduction of trap density in these systems, such doping sites can also act as localisation centres to increase the intrinsic radiative recombination rate.

## **Chapter 3: Methods**

In this chapter the methods are briefly discussed which were employed to investigate the perovskite-based semiconductor systems studied within this thesis in the following chapters. We will start with an overview of photoluminescence-based experiments, and will then focus on absorption-based measurements – both experiments can be performed in a steady-state and time-resolved manner. The chapter concludes with supporting methods that were used in collaboration with other researchers to draw a detailed picture of the working mechanism of charge localisation in perovskites.

## 3.1 Photoluminescence-based experiments

As we discussed in the previous chapter, studying optical transitions in semiconductors is of major interest to quantify the performance of device applications based on these materials. In photoluminescence experiments, the sample is excited with a light source, which – depending on the photon energy chosen – will promote an electron from the valence to the conduction band. As one possible de-excitation pathway, the electron can relax back into the valence band under emission of a photon, which can then be detected.

While quantifying the efficiency of this process is possible through steady-state measurements, in order to gain a mechanistic understanding of the charge carrier dynamics, time-resolved methods are required. We will discuss the most important of these methods which I used throughout my PhD in the following sections.

## 3.1.1 Photoluminescence quantum efficiency measurements

Photoluminescence quantum efficiency (PLQE, often also found in the literature as yield, PLQY) measurements were conducted to establish the ratio of radiative decay to non-radiative decay in photoexcited perovskite films. Excitation for the experiments described in Chapter 4 and 5 was provided by a continuous wave diode laser (Thorlabs L520P50, 2.38 eV photon

energy). As outlined by De Mello et al. [112], three measurements were made on each sample to establish the external PLQE at a given excitation fluence. The samples were housed in an integrating sphere to collect all PL and any reflected or transmitted laser light, which was then fibre-coupled to an Andor Shamrock spectrometer and Andor iDus DU420A-BVF CCD array. A corrected value is then determined by collecting the light from the sphere without a sample, without hitting the sample and with hitting the sample, respectively. This procedure allows one to account for scattering or reabsorption of the sample which might otherwise result in a wrong PLQE result. Stated values were determined on triplicate samples which were each measured twice, hence reporting the average of six measurements for each composition to obtain reliable results.

## 3.1.2 Transient photoluminescence spectroscopy

Transient photoluminescence (PL) is a powerful tool to study radiative recombination in semiconductor systems. The preferred experimental technique and repetition rate depend on requirements such as desired time resolution and excitation density as well as the maximum lifetime of the sample. Whilst time-correlated single-photon counting (TCSPC) or the use of an intensified charge-coupled device (iCCD) offer well-established and commercially readily available methods for long-time measurements (time resolution of > 100 ps), the ultrafast time range below 1 ps is experimentally more challenging. Typical methods for this regime include photon up-conversion and Kerr gating [113]. In our lab, a transient grating-based setup is used for this ultrafast regime, which I employ frequently to also measure luminescent materials in collaborative work. Even though this time regime was not of primary importance for the studies discussed in Chapters 4 and 5, I would therefore still like to discuss its general concept and the interested reader is welcome to find more details of results employing this technique in the attached list of publications.

Figure 20 summarises the time range typical for each setup, and I will briefly discuss the working principle of each of them in the following.


Figure 20: Time ranges (logarithmic) of photoluminescence decays and respective techniques suitable to measure them. A transient grating is utilised to cover the ultrafast regime (100 fs - 1 ns), TCSPC can be used to cover the 100 ps - 800 ns range, while the iCCD covers time scales from approximately 1.5 ns out to 1 ms.

Conceptually, in transient photoluminescence the sample of interest (in our group mostly novel organic or perovskite semiconductors) is excited with short laser pulses, as shown in Figure 21.



Figure 21: Working principle of transient photoluminescence spectroscopies. A sample is being photo-excited with a pump pulse and subsequently emits light. This photoluminescence is being collected and focussed onto a spectrometer to disperse the different wavelengths, e.g. with a grating. The time-resolved (TR) gate allows to monitor the photoluminescence at a given time delay after the excitation pulse arrives and the detector (e.g. a charge-coupled device) reads out the intensity signal of the measured photons. Its exact position and form depends on the setup. L: lens, M: mirror, SM: spherical mirror, I: iris, LP: long-pass filter, SP: short-pass filter.

The resulting photo-excited states within the measured material then decay with distinct lifetimes back to the ground state or another state of lower-lying energy, e.g. a triplet state. This decay can be non-radiative, dissipating heat, or radiative, under emission of light which is measured. In order to measure the intensity of the spectrum at each wavelength, the light

emitted from the sample is first collected and focused onto a spectrometer, which consists of a prism or grating to disperse it. After the wavelength separation, the intensity (or number of photons) of each wavelength can then be measured with a detection unit. The latter ultimately makes use of the photoelectric effect [114] in order to convert the optical signal to an electrical signal which can be measured. A gating of either electrical (like in TCSPC or an iCCD) or optical origin (like in transient grating PL) can furthermore be applied to measure the PL signal as a function of time delay after photoexcitation to gather information about the kinetics of the excited electronic states, as described for the different experimental realizations in the following section.

### **3.1.2.1** Time-correlated single-photon counting

The first time-resolved method to detect photoluminescence decays discussed here is timecorrelated single photon counting (TCSPC), since its principle of operation [115] is fundamentally different from the other gated methods. TCSPC is a transient PL measurement based on a 'time-of-flight' method, as illustrated in Figure 22.

The time delay between emission of a pump pulse and arrival of the first PL photon from the emitting sample is measured. The so acquired time-of-flights are then sorted in a histogram which – after many repetitions – will eventually reflect the decay dynamics of the emitting sample.

TCSPC measurements are typically performed without spectral resolution. However, spectral resolution can be achieved by using a monochromator in the detection beam path and by performing individual TCSPC scans for each detection wavelength, so called time-resolved emissions scans (TRES). This increases the experimental time significantly so that iCCDs are often the faster tool, if spectral resolution is desirable and the time-resolution is suitable.



Figure 22: Working principle of time-correlated single-photon counting (TCSPC). The arrival of the excitation laser pulse instigates the electronic timer, while detection of an emitted photon stops it. Over many measurement cycles a histogram can be reconstructed from the individual start-stop time delays, which describes the photoluminescence kinetics of the sample (here: logarithmic plot of individually counted photons describing an exponential decay). L: lens, M: mirror, SM: spherical mirror, I: iris, LP: long-pass filter, SP: short-pass filter, APD: avalanche photodiode.

The sample is excited with a pulsed laser at a repetition rate which is chosen to be small enough to monitor the complete photoluminescence decay before the next pulse arrives. Pump scatter light from the laser excitation within the photoluminescence path to the detector was filteredout using absorptive long-pass filters with e.g. with a 425 nm edge when using a 405 nm laser. The detection wavelength is then selected using the slit of a monochromator in front of the spectrometer. The photoluminescence is then focused and detected by a single-photon avalanche photodiode based on Si (MPD-PDM-PDF) with an instrument response of ~100 ps. TCSPC measurements can by design only detect one photon per repetition. They thus require high repetition rates on the order of MHz in order to build up a representative histogram. For samples with long lifetimes like perovskite semiconductors or phosphorescent emitters, iCCDs are preferable as they allow to detect more than one photon per repetition. Therefore, they can be operated at lower repetition rates.

#### **3.1.2.2** Intensified charge-coupled devices

iCCDs are charge-coupled device cameras with an intensifier unit in front of them that multiplies the number of incoming photons and allows an electronic gating of the signal at the same time. In contrast, electron-multiplying charge-coupled device (emCCD) relies on multiplication of the electrons after detection of light in the charge-coupled device chip.

For an iCCD, the PL light is first dispersed in a spectrometer before it is absorbed in the photocathode of the intensifier unit, depicted in Figure 23.



Figure 23: Working principle of the intensifier unit in a charge-coupled device (CCD) camera. The photocathode converts incoming photons to photoelectrons, which are strongly multiplied by the microchannel plate. The phosphor screen then converts these multiplied electrons back to an amplified number of photons to be detected by the CCD chip that follows after the output window.

The photoelectrons are then drawn into the honeycomb-structured microchannel plate (MCP). A high voltage accelerates the photoelectrons in the channels of the MCP causing impact ionization at the channel walls and thus a multiplication of the number of electrons. The voltage intensity across the MCP controls the intensification level. After the MCP, the electrons hit a phosphor screen that converts the electrons back into light which is then detected by the charge-coupled device. The strength of an iCCD lies in the MCP: Its separated channels allow to achieve spectral resolution, since the incoming light was already dispersed in the spectrometer. Furthermore, due to the requirement of an accelerating voltage, light detection of the camera can be controlled by switching the voltage on and off. iCCDs therefore allow a gating of PL emission by triggering the MCP voltage using a digital delay generator to set the desired delay time after the laser pulse excites the sample. The time resolution is here only limited by the system's RC constant. iCCDs thus achieve time resolutions of 200 ps or longer.

Steady-state and time-resolved photoluminescence measurements described in Chapter 4 about photo-doping in alloyed perovskites were taken with the iCCD camera system Andor iStar DH740 CCI-010 connected to a grating spectrometer (Andor SR303i). Excitation was realised

through femtosecond laser pulses generated in a homebuilt setup by second harmonic generation (SHG) in a BBO crystal from the fundamental output (pulse energy 1.55 eV, pulse length 80 fs) of a Ti:Sapphire laser system (Spectra Physics Solstice). The laser pulses had an energy of 3.1 eV. Temporal resolution of the PL emission was obtained by measuring the PL from the sample and stepping the iCCD gate delay for different delays with respect to the excitation. The best achievable time resolution of our iCCD is about 4 ns as determined via measuring the instrument response of the iCCD to a 100 fs laser pulse.

For temperature-dependent measurements, sample temperature was maintained in a cold finger cryostat, under vacuum. Constant liquid helium flow through the heat exchanger, and a temperature controller connected to a copper filament heater allowed for temperature regulation and stabilisation.

#### **3.1.2.3** Ultrafast photoluminescence experiments

To enable the study of early-time carrier dynamics in perovskites and other organic or inorganic semiconductors, a setup is required that can resolve ultrafast kinetics on the sub-ps timescale, while preferably allowing the user to monitor the whole PL spectrum at each time delay in order to capture spectral changes. Common examples of ultrafast PL techniques that allow for time resolutions in the femtosecond-regime include Kerr gating [113], photon up-conversion or streak cameras [116]. The first two rely on optical gating methods, in contrast to an iCCD which uses an electronic gate. These optical gating experiments are summarised in Figure 25, of which in our lab the third, transient-grating-based method is used.

Photon up-conversion measurements are based on up-converting PL photons to a higher energy via sum-frequency generation together with a gate photon in a birefringent crystal. The higher energy of the up-converted photons allows them to be subsequently distinguished spectrally from the background PL. By tuning the time delay between the pump pulse and the gate pulse with a mechanical delay stage, the time-dependent evolution of PL spectra can be measured. Since photon up-conversion requires phase matching, i.e. all wavelengths travelling with the same velocity through the crystal medium, the detection window is limited to a narrow range of PL wavelengths. Furthermore, a fine spectral calibration is necessary, as the up-conversion efficiency drops significantly at the edges of the phase matching window. However, this

window can be broadened by scanning the crystal's angle to recover the phase-matching condition.



Figure 24: Different techniques to enable ultrafast photoluminescence measurements. (a) Fluorescence upconversion, where sum-frequency generation is used to separate the gated PL from the background. (b) Optical Kerr gating, which separated the gated PL signal from the background through a change of polarisation. (c) Transient grating PL spectroscopy, used in our lab, creates a transient grating through refractive index modulation according to the interference pattern of two gate beams to deflect the gated PL from the background and spatially separate it, while being detecting still the whole spectrum. Reproduced with permission from ref. [116].

Optical Kerr gate spectroscopy uses a laser-induced change in polarisation of the PL to distinguish the signal from the background. A 'Kerr medium', for example fused silica, is placed in between two cross-polarized polarizers. The PL passes through the first polarizer onto the Kerr medium and eventually is blocked by the second polariser. If now a strong gate pulse is shone onto the Kerr medium, the optical Kerr effect will cause a refractive index change in the medium causing birefringence and thus a rotation of the polarisation of the PL. The rotated PL signal can then pass through the second polariser. Kerr gating setups work well with low repetition rate lasers but suffer from a high background level. This is set by the

extinction ratio of the polarisers and thus leakage of background PL light through the polarisers is particularly problematic for measuring long-lived samples.

Recently, Chen *et al.* discussed studying ultrafast photoluminescence based on a transient grating optical gate [116], which combines the low background detection of up-conversion with the broadband phase-matching capability of optical Kerr gating. For this method, two gate beams are focussed onto a Kerr medium causing an interference pattern and thus an optical Kerr effect at the positions of interference maxima. This results in a transient grating with periodically changing refractive index in the gate medium. The PL light is then being focussed onto the transient grating and deflected according to the law of diffraction. This technique thus relies on a spatial separation of the signal from the steady-state PL background. Figure 25 illustrates the experimental setup used in Cambridge.



Figure 25: Experimental setup for transient grating photoluminescence spectroscopy. The sample which was photoexcited with a pump pulse emits photons which are optically gated via a transient grating. The latter only exists for the duration of two gate beams overlapping in space and time on a Kerr medium whose refractive index is modulated in accordance with the interference pattern by means of the optical Kerr effect. The deflected and thus spatially separated photoluminescence signal can then be detected by an iCCD camera as the detector unit. L: lens, M: mirror, SM: spherical mirror, I: iris, LP: long-pass filter, SP: short-pass filter.

The transient grating setup allows a 100 fs time-slice of PL to be measured with an ultralow steady-state PL background, if a high-quality gate medium is chosen (in our case a highly polished piece of fused silica), and is thus ideally suited to measure samples with short PL lifetimes. Furthermore, it allows for broadband phase matching due to the focussing of the gate beams which provides a wide range of gate vectors. More information on this method can be found in ref. [116].

#### 3.1.3 Confocal photoluminescence microscopy

Confocal photoluminescence microscopy [117] is a useful method for mapping fluorescence (photoluminescence) of molecules or semiconductors with high spatial resolution, and Figure 26 illustrates its concept. In contrast to wide-field microscopy, the confocal microscope does not illuminate the whole sample at once, but instead employs a focused laser beam as excitation source. The emission arises therefore predominantly from a specific location in the sample and in the focal plane. A pinhole in the back focal plane then blocks any light coming from outside the focal plane, thus only photoluminescence from the illuminated sample spot can enter the detector. By scanning the sample in a raster pattern (in all three spatial dimensions, if desired), the full sample emission can be mapped out at diffraction-limited resolution (~300 nm in our case). The detector can in principle have the form of any of the techniques discussed above. In our setup a common CCD chip is used for spectral information, which can be exchanged for a TCSPC detector in order to record kinetics.



Figure 26: Illustration of a confocal microscopy setup. The pinhole restricts the observed sample volume, i.e. the local photoluminescence, to a single point, limited by the pinhole size. Excitation by a laser pump beam with source optically conjugated to the pinhole is focused to a diffraction-limited spot.

Photoluminescence maps shown in Chapter 4 were acquired by Gregory Tainter and myself using a WITec alpha 300s setup. The excitation source was a 405 nm continuous wave laser (Coherent CUBE) with a fluence of 6 W cm<sup>-2</sup>. The light was coupled though an optical fibre to the microscope and focused using a 100x Nikon lens (NA = 0.95, spot size 1.5  $\mu$ m). Samples rested on an X-Y piezo stage of the microscope. The PL signal was collected in reflection mode with the same 100x objective and detected using a Princeton Instruments SP-2300i spectrometer fitted with an Andor iDus 401 CCD detector. A long-pass filter with a cut-off wavelength of 450 nm was used to block the excitation. The PL peak energy was determined from the spectrum at each position using a centre of mass fit.

## **3.2 Optical absorption measurements**

In order to reach a comprehensive picture of the charge carrier dynamics in semiconductors, it is important to not only quantify the fraction of charges recombining radiatively – as detected with photoluminescence – but also measure the ability of the material to absorb light in the first place. In principle, both transitions are fundamentally connected via the Einstein relations [19], yet in reality non-radiative loss mechanisms will often lead to a divergence between absorption and spontaneous emission. In this section we will discuss how absorption-based experiments allow us to track the excited charge-carrier population in semiconductors, as used in the following chapters, and thus to distinguish between radiative and non-radiative decay channels when compared to photoluminescence measurements. Together, these optical experiments help us to identify the performance of the studied semiconductors for optoelectronic applications.

#### **3.2.1** Steady-state absorption

A Shimadzu UV-3600 Plus spectrophotometer was used to collect the steady-state absorbance spectra of samples, which uses a photomultiplier tube. The final data shown in Chapters 4 and 5 are corrected for by measuring first the pristine substrate (films in Chapter 4) or cuvette with the solvent (toluene solutions for Chapter 5) only, and then subtracting this spectrum from the one with the perovskite, respectively.

#### **3.2.2** Transient absorption

With transient absorption (TA) spectroscopy, the electronic structure of materials that interact with light can be studied. Specifically, for my work on charge localisation and accumulation in perovskites, this technique was used to monitor the total carrier density over time after photo-excitation. In the following, we will first discuss the general concept of transient absorption, and then discuss some specifics of the experimental setup used in Cambridge.

#### **3.2.2.1** Concept of transient absorption

In TA, the changes in the absorption spectra of a sample after excitation with a first laser pulse is measured through a time-delayed second pulse. More accurately, in our group we monitor the change in transmission ( $\Delta T$ ) rather than absorption. Since organic semiconductors, like polymers or small molecules, have generally a small refractive index, the contributions from transmission signals that are not from absorption of the sample are often negligible here. For hybrid perovskites with a relatively high refractive index, however, one must be carefully keeping in mind the difference between both observables, as e.g. demonstrated by Price et al. [94].

Generally, the change in transmittance through a sample will depend on both the absorbance and reflectance of that sample via:

$$T = 1 - A - R \tag{62}$$

with the transmission *T*, absorption *A*, and reflection *R*. The occupation of bands with charges directly influences the dielectric constant of the material, which is a complex function. The imaginary part of this relative permittivity  $\varepsilon(\omega)$  is directly proportional to the absorption coefficient  $\alpha(\omega)$  via:

$$\alpha(\omega) = \frac{\omega}{nc} \operatorname{Im}[\varepsilon(\omega)]$$
(63)

where  $\omega$  is the radial frequency of light, *c* is its speed in a vacuum, and *n* is the refractive index. The promotion of an electron from the valence to the conduction band upon photon-absorption by can then lead to a change in the dielectric function, i.e. of the complex refractive index, which impacts both the absorbance and reflectance of the following photons interacting with the sample, thus influencing the measured transmission. The Kramers-Kronig relations [118,119] can in principle be applied to extract the real or imaginary part (i.e. the absorption coefficient) from the complex refractive index, if either of them is known. With these general relations in mind, let us now discuss their consequences for a so called 'pump-probe' experiment where one light pulse is followed by a second, time-delayed one, and how this can be useful to gather information on the carrier dynamics of a semiconductor.

Ultrafast TA can be used to measure changes on up to femtosecond time scales, utilising short laser pulses. As depicted in Figure 27, a short laser pulse of rather narrow wavelength – the pump beam – arrives and excited the sample at time t = 0. Then, at a varied time delay, a (usually) broadband pulse – the probe beam – arrives at the same spot on the sample, passing through it and being detected subsequently with its modulated intensity.



Figure 27: Illustration of transient absorption spectroscopy. A pump beam excites the sample, which is then probed with a variable time delay by a white light probe beam. The change of transmission of the probe is measured at the detector unit.

Often, a reference probe beam, split from the main probe beam through a beam splitter, is also directed onto the sample – but on a different spot than pump and sample probe. Detecting the intensity of this reference probe allows to correct for shot-to-shot differences in the probe beam. The change in measured probe intensity as a function of time and wavelength of the spectrum is conventionally represented by the fractional differential transmission:

$$\frac{\Delta T}{T} = \frac{T_{Pump \ on} - T_{Pump \ off}}{T_{Pump \ off}} \tag{64}$$

Here, *T* denotes the transmitted probe beam intensity (as opposed to the temperature like in the previous chapter), and  $T_{Pump \ on}$  and  $T_{Pump \ off}$  are the intensities with and without exciting the sample through a pump beam before, respectively. Each of these intensities is also divided by the reference probe intensity, if applicable, to reduce shot-to-shot noise.

In transient absorption, one can typically observe a selection of characteristic features, shown in Figure 28, which offer valuable information over the electronic structure of photoexcited materials.



Figure 28: Characteristic electronic transitions observable in transient absorption (TA). A ground state of singlet character ( $S_0$ ) can be bleached upon photo-excitation meaning less probe light will be absorbed by it, which results in a positive ground-state bleach (GSB) signal. Furthermore, the singlet first excited energy state  $S_1$  can be stimulated to emit through the probe, also resulting in a net increase in detected light and hence positive signal, based on stimulated emission (SE). The first excited singlet state can also absorb light and be excited higher in energy (e.g. to the second excited singlet state  $S_2$ ), which reduces the amount of transmitted light and results in a negative TA signal. Adapted from ref. [120].

Considering the ground state of an organic molecule to be a singlet ( $S_0$ ), or similarly an electron of an inorganic semiconductor at the valence band maximum, then photoexcitation with a pump pulse of energy equal to or greater than the material's bandgap will result in exciting it to the appropriate higher-lying electronic state, e.g. a singlet  $S_1$ , or the electron being promoted to the conduction band minimum. Probe light that was formerly absorbed by the ground state will now be transmitted to a greater extent due to the missing ground state absorbing species in presence of the pump beam and the net increase in measured TA signal is referred to as a ground-state bleach (GSB). Furthermore, the resulting excited species, can be stimulated by the perturbation of the electric field through the probe pulse to relax under light emission, yielding a higher photon count at the detector than without the pump excitation, which also results in a positive TA signal, this time due to stimulated emission (SE). Lastly, the excited electronic state initially generated by the pump pulse may also absorb probe light to be promoted to even higher-lying electronic states, resulting in a reduced transmitted probe intensity, which is referred to as photo-induced absorption (PIA).

It is worth emphasising again, that especially for the investigation of hybrid perovskite materials, also other effects contribute significantly to the measured TA signal. For example, one typically observes a photo-induced refractive index change, meaning that for the duration of the sample being excited, it transiently also changes its reflectivity, as discussed above. Here, one generally observes a negative TA signal at higher energies than the ground-state bleach, with the same kinetics as the GSB; work that has been extensively studied by Price et al. in our group [94]. Furthermore, derivative features can also be observed, such as electro-absorption, which results from a transient photo-induced form of the Stark effect, wherein the absorption spectrum is perturbed by an internal electric field. By expanding the change in absorption coefficient as a function of electric field in a Taylor series, a quadratic Stark effect emerges [121]. This decreases the energy of electronic states with small intrinsic dipoles, resulting in a small redshift of transmitted probe spectrum and hence a derivative-type feature in TA. Other origins of photo-induced transmission changes include many-body effects like bandgap renormalisation, thermal and pressure effects.

#### **3.2.2.2** Experimental setups for measuring transient absorption

In our labs, transient absorption measurements can be carried out on several different setups to cover timescales ranging from  $\sim 80$  fs to several ms and wavelengths from the ultraviolet to the infrared. The modular home-built systems are depicted in Figure 29.



Figure 29: Experimental transient absorption setups in the Optoelectronics group in Cambridge. a) shows the optical alignment of pump an probe sources, where mirrors (*I*) are interchanged to select pump sources and mirrors (*II*) are interchanged to select probe sources. (*III*) is a beamsplitter utilised to generate the second reference probe beam. b) Schematic of a broadband non-collinear parametric amplifier (NOPA). BS: beamsplitter, VA: variable attenuator, L: lens, SM: spherical mirror, DS: delay stage, NLC: non-linear crystal. Reproduced from ref. [122].

For both ultrashort and short-time TA both the pump and probe lasers are seeded from the same laser source. It consists of a Spectra Physics MaiTai Ti:Sapphire oscillator which generates femtosecond pulses. Those are stretched and amplified in an amplifier unit (Spectra Physics Solstice, pumped by an Empower) through chirped pulse amplification, and then compressed again, before they are ejected via the Q-switching mechanism in a Pockels cell. The resulting 800 nm pulses at a repetition rate of 1 kHz with about 100 fs pulse duration is then split to pump both the probe and pump paths. For short time TA the pump is a tunable optical parametric amplifier of super-fluorescence (TOPAS, Light Conversion), which can be tuned to wavelength outputs between 200 and 2000 nm. After passing through an optical chopper, on- and off-shots of the pump have a repetition rate of 500 Hz. The pump beam then passes through a halfwave plate to ensure that the angle between the directions of linear polarization between pump and probe is at the desired 'magic angle' of  $arccos(1/\sqrt{3}) = 54.7^{\circ}$ , where the signal is independent of the dipole orientation in the sample (at least in an idealised liquid sample). An ND filter wheel allows to control the intensity of the pump beam before it arrives at the sample position [123]. Alternatively, the 800 nm can also be used to generate a simple

400 nm pump beam by sending it through a frequency-doubling  $\beta$ -barium borate ( $\beta$ -BaB<sub>2</sub>O<sub>4</sub>, BBO, the only phase used throughout this thesis) crystal.

The other part of the 800 nm beam pumps the broadband probe generation realised through a non-collinear optical parametric amplifier (NOPA) modelled on Cerullo et al. [124]. Figure 30 shows a photo of such a NOPA in our group and beam paths are highlighted.



Figure 30: Photograph of a non-collinear parametric amplifier (NOPA) in the Optoelectronics group in Cambridge. Red lines show the 800 nm beam path, yellow lines the white light supercontinuum, blue lines the 400 nm pump line, and orange the resulting broadband probe beam used for transient absorption spectroscopy. Photograph kindly provided by J. M. Richter.

The visible (ca. 450-800 nm) and near-infrared (ca. 800-1100 nm) NOPAs make use of a sapphire crystal to generate a white light (WL) supercontinuum, as well as two (or one) BBO crystal(s) to amplify this WL through non-linear processes. For the visible range the 800 nm beam is frequency-doubled by a first BBO crystal creating a 400 nm pump pulse, that is aligned spatially to focus together with the WL seed at an angle close to 3.7° onto the second BBO crystal, whilst being overlapped temporally using a mechanical delay stage. The WL pulse is likely generated via extreme self-phase-modulation resulting from very intense spatial solitons created by the interplay of self-focusing and local ionisation [125]. The overlap of the pump and seed in the non-linear medium then is used to define the amplified spectrum depending on the phase-matching between both pulses.

To probe the kinetics of the photo-excited system, the probe beam is being delayed using a motorized mechanical delay stage with a retroreflector mounted on it, before being split into

probe and reference beams that pass through the sample and are being coupled into an imaging spectrometer with an iCCD camera. For the near-infrared region, a periodically poled stoichiometric lithium tantalate crystal is used rather than a BBO crystal to amplify the WL spectrum. Details on this setup can be found in the literature [122]. For long-time TA experiments, instead of using a TOPAS or direct 400 nm pump, a Q-switched pulsed laser (Advanced Optical Technologies) with Nd:YVO<sub>4</sub> as gain medium is used, emitting temporally synchronised pulses at 532 nm and 500 Hz repetition rate. The nominal pulse duration is 600 ps and the delay can be electronically controlled, allowing time ranges from about 1 ns to ca. 1 ms to be measured when combined with the probe pulses described above.

Specifically for the charge accumulation studies discussed in Chapter 4, the second harmonic of a pulsed Nd:YVO4 laser (AOT-YVO-25QSPX) was used as the pump beam (500 ps pulse width, 500 Hz repetition rate, 2.33 eV photon energy). The probe spectrum was generated using the home-built noncolinear optical parametric amplifier described above, pumped by the second harmonic of the same Ti:Sapphire amplifier (Spectra-Physics Solstice). A delay generator was used to electronically vary the pump-probe delay. Transmitted probe and reference pulses were recorded with an NMOS linear image sensor (Hamamatsu S8381-1024Q) and processed by a customized PCI interface from Entwicklungsbüro Stresing.

Similarly, for the exciton localisation studies in Chapter 5, the third harmonic of a pulsed Nd:YVO<sub>4</sub> laser (Picolo-AOT MoPa) was used as the pump beam (1 ns pulse width, 500 Hz repetition rate, 355 nm) for the ns regime measurements. The probe spectrum was generated using a white light quasi-continuum generated through pumping a CaF<sub>2</sub> window with the 800 nm fundamental. A delay generator was used to electronically vary the pump-probe delay. For the short time fs-regime, the pump beam was the second harmonic (400 nm) generated by the 800 nm fundamental passing through a  $\beta$ -barium borate crystal. Transmitted probe and reference pulses were recorded in the same way as described above.

## **3.3** Electron probe microanalysis

Electron probe microanalysis (EPMA) is a setup in Cambridge based on an electron microscope. The electron beam is used to scan a sample, and at each position the element-specific X-ray fluorescence induced by the inelastic scattering from the electron beam is

analysed. In Chapter 4, this method is used to detect the local ratio of iodide and bromide ions in the perovskite sample.

EPMA maps shown in Chapter 4 were measured by Stuart Macpherson, Tiarnan Doherty, Iris Buisman and Emilie Ringe with a Cameca SX100 at the Earth Sciences Department, University of Cambridge. A 15 kV electron beam with a probe size of 1 µm was used with a current of 20 nA. I and Br were analysed on peak on layered pentaerythritol (LPET) and layered thallium acid phthalate (LTAP) crystals respectively. Each pixel in the elemental maps was acquired with a 300 ms dwell time (longer dwell times were avoided to prevent sample damage), with a step size of 500 nm.

### **3.4** Transistor experiments

In the following, the transistor fabrication and measurements for the multi-cation and mixedhalide perovskite thin films are described that were used for Chapter 4. Transistors were fabricated by Satyaprasad Senanayak and Henning Sirringhaus.

In brief, bottom gate bottom contact perovskite field effect transistors were fabricated using Si/SiO<sub>2</sub> (300 nm) substrate on which Cr/Au source drain electrodes (25 nm) are lithographically patterned with channel length of 100  $\mu$ m and width of 1mm. Perovskite thin films were spin coated at 5000 rpm for 180 seconds using standard antisolvent technique as used for the spectroscopic measurement to obtain films of thickness ~150 nm. The devices were then annealed for 30 minutes at 100 °C. All the devices were characterized in a vacuum chamber (10<sup>-6</sup> mbar) using an Agilent 4155B parameter analyser, operated in pulsed mode. For the transfer measurement,  $V_g$  was applied over a short impulse of 0.5 ms and the transfer characteristics were measured. For the photo-illumination study, the device was illuminated from the top with an intensity controllable white light source with a maximum intensity of 10 mW cm<sup>-2</sup>. The interfacial charge density is given by the expression:  $Q = C_i (V_g - V_{th})/e$  where *C* is the capacitance per unit area,  $V_{th}$  is the threshold voltage,  $V_g$  is the maximum gate voltage and *e* is the unit electronic charge. Photoinduced charge density is then estimated from the shift in  $V_{th}$  obtained by comparing the dark transfer characteristics with transfer characteristics obtained after illumination.

## **3.5** Structural characterisation (TEM and XRD)

The morphologies of the perovskite nanocrystals studied in Chapter 5 were characterised structurally by Mahesh Gangishetty, using a JEOL ARM 200F scanning-transmission electron microscope (STEM, 80 kV). X-ray diffraction (XRD) data was acquired by a Bruker D2 Phaser.

### **3.6 Sample Fabrication**

In this section I will briefly describe the preparation of the perovskite-based samples used for the studies in Chapter 4 and 5. For Chapter 4, mixed-cation mixed-halide alloys were used to fabricate thin films, while in Chapter 5, colloidal solutions of mixed-halide inorganic perovskite nanocrystals were synthesised.

#### 3.6.1 Thin films of bulk perovskites for charge accumulation studies

In the following, the sample fabrication for the multi-cation and mixed-halide perovskite thin films is described that were measured in Chapter 4. Sample preparation was carried out by Stuart Macpherson, Satyaprasad Senanayak, Mojtaba Abdi-Jalebi, Kyle Frohna, and myself. Lead compounds were purchased from Tokyo Chemical Industry. Organic cation salts were purchased from GreatCell Solar. Cesium iodide, potassium iodide and rubidium iodide were ordered from Alfa Aesar. Subsequent materials were purchased from Sigma-Aldrich. Precursor solutions for the mixed halide samples were produced by first dissolving PbI<sub>2</sub> (1.1 M) and PbBr<sub>2</sub> (0.22 M) in a mixture of anhydrous DMF and DMSO (4:1 v:v). The following additional steps were carried out to produce the respective compositions: MAPb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> perovskite: add 1 M MAI and 0.2 M MABr. MA<sub>0.17</sub>FA<sub>0.83</sub>Pb(I<sub>0.83</sub>Br<sub>0.16</sub>)<sub>3</sub> perovskite: add 1 M FAI and 0.2 M MABr. Cs<sub>0.06</sub>MA<sub>0.15</sub>FA<sub>0.79</sub>Pb(I<sub>0.84</sub>Br<sub>0.16</sub>)<sub>3</sub> perovskite: add 1 M FAI and 0.2 M MABr. Dissolve 1.5 M CsI in DMSO. Add CsI solution to precursor solution in 5% volume ratio (5:95 v:v). Rb<sub>0.05</sub> / Cs<sub>0.05</sub>(MA<sub>0.15</sub>FA<sub>0.79</sub>)<sub>0.95</sub>Pb(I<sub>0.84</sub>Br<sub>0.16</sub>)<sub>3</sub> perovskite: as for CsMAFA. Dissolve 1.5 M RbI in a mixture of DMF:DMSO 4:1 (v:v). Add

RbI solution to CsMAFA solution in 5% volume ratio (5:95 v:v).  $K_{0.1}/Cs_{0.05}(MA_{0.15}FA_{0.79})_{0.95}Pb(I_{0.84}Br_{0.16})_3$  perovskite: as for CsMAFA. Dissolve 1.5 M KI in a mixture of DMF:DMSO 4:1 (v:v). Add KI solution to CsMAFA solution in 10% volume ratio (10:90 v:v). Bare perovskite films were spin-coated using a two-step procedure in a nitrogen atmosphere. Precursor solutions were deposited on glass cover slides and spun at 2000 rpm for 10 seconds, then 4000 rpm for 35 seconds. 150 µL of chlorobenzene was added 30 s after commencement of the procedure. Films were annealed at 100 °C for one hour.

MAPbI<sub>3</sub> films were prepared based on the protocols of Liu et al. [126]. Glass slides were coated with 60  $\mu$ l of a 1.5 mg mL<sup>-1</sup> solution of Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA, EM Index, MW = 19,000) in toluene (Sigma-Aldrich) using a two-step spin coating procedure: 500 rpm for 4 s, then 4500 rpm for 20 s. PTAA films were annealed at 70°C for ten minutes. MA-I precursor solutions were prepared by dissolving anhydrous 0.6 M Pb(CH<sub>3</sub>COO)<sub>2</sub> (TCI), 0.067 M PbCl<sub>2</sub> (Sigma), 2M MAI (Greatcell Solar) and 0.067M DMSO (Sigma-Aldrich) in DMF (Sigma-Aldrich). The MA-I solution was heated to 75 °C during film deposition. 100  $\mu$ L of solution was deposited and spun at 2000 rpm for 10 s, then 6000 rpm for 30 s. The films were annealed at 75°C for two minutes then capped with a layer of poly(methyl methacrylate) (Aldrich, M<sub>w</sub> = 996,000), 30 mg mL<sup>-1</sup> in chlorobenzene (Sigma-Aldrich). 60  $\mu$ L was deposited on the MA-I film and spun at 4000 rpm for 30 s before drying at 75 °C for five minutes.

# **3.6.2** Synthesis of pristine and Mn-doped perovskite nanocrystals for localisation studies

In the following, the synthesis of the nanocrystals studied in Chapter 5 is described. Synthesis was carried out by Mahesh Gangishetty.

The detailed synthesis of undoped and Mn-doped perovskite nanocrystals can be found in ref. [110] and the literature cited therein. Briefly, for undoped CsPb(Cl,Br)<sub>3</sub> nanocrystals, 165 mg of PbBr2 (0.450 mmol, purity 98%), 83.6 mg of PbCl<sub>2</sub> (0.301 mmol, purity 98%), 20 mL of octadecene, 2 mL of oleylamine (purity 98%), 2 mL of oleic acid, and 2 mL of trioctylphosphine (purity 97%) were loaded into a 100-mL three-neck flask, dried under vacuum at 130°C for 45 min, and heated to 150°C under stirring. The yielded clear solution was heated to 165°C under N<sub>2</sub> protection, after which 1.7 mL of pre-heated Cs-oleate

precursors was swiftly injected into the solution. After reacting for 10 s, the product was cooled to room temperature in an ice/water bath. Synthesis of low Mn<sup>2+</sup>-doped perovskite nanocrystals (1‰ from ICPMS) involved loading 210 mg (0.572 mmol) of lead(II) bromide (PbBr<sub>2</sub>, purity 98%), 50 mg of manganese(II) chloride (MnCl<sub>2</sub>, purity 99.999%), 20 mL of octadecene, 2 mL of oleylamine (purity 98%), 2 mL of oleic acid, and 2 mL of trioctylphosphine (purity 97%) into a 100-mL three-neck flask. This was dried at 130°C for 45 min and heated to 150°C under vacuum. The yielded solution was then heated to 165°C under N<sub>2</sub> protection, after which 1.7 mL of pre-heated Cs-oleate precursors was rapidly injected into the solution. After having reacted for 10 s, a crude product was cooled to room temperature in an ice/water bath. Synthesis of high Mn<sup>2+</sup>-doped perovskite nanocrystals (1.9‰ and 2.5‰ nomenclature) was the same as for the low-doped synthesis, except more MnCl<sub>2</sub> was used (70 mg and 80 mg of MnCl<sub>2</sub> precursor, respectively).

## 3.7 Computational methods

In this section, the computational methods based on density functional theory are outlined that were used to support the experimental findings discussed in Chapters 4 and 5.

#### 3.7.1 Computational details for charge accumulation studies

In the following, the computational methods for the multi-cation and mixed-halide perovskite heterojunctions are described that were calculated in Chapter 4. The modelling was carried out by Guangjun Nan and David Beljonne.

The heterojunctions adopted in this work are based on cubic phases of MAPbI<sub>3</sub> [127], MAPbBr<sub>3</sub> [127], FAPbI<sub>3</sub> [128] and FAPbBr<sub>3</sub> [129]. For the cubic FAPbI<sub>3</sub>/MAPbI<sub>3</sub> heterojunctions, the lattice constant is 25.38 Å, which introduces a lattice mismatch of only - 0.24% and +0.24% for FAPbI<sub>3</sub> and MAPbI<sub>3</sub>, respectively. For the cubic MAPbI<sub>3</sub>/MAPbBr<sub>3</sub> heterojunctions, the lattice constant is 24.46 Å, which yields a lattice mismatch of -3.4% and 3.6% for MAPbI<sub>3</sub> and MAPbBr<sub>3</sub>, respectively. As far as the cubic MAPbBr<sub>3</sub>/FAPbI<sub>3</sub> and MAPbI<sub>3</sub>/FAPbBr<sub>3</sub> heterojunctions are concerned, the chosen constant (24.58 Å) is setup by averaging the lattice parameters of the 4×4×4 supercells for MAPbI<sub>3</sub>, MAPbBr<sub>3</sub>, FAPbI<sub>3</sub> and FAPbBr<sub>3</sub>, which then gives the lattice mismatch of -2.9%, 4.2%, -3.4% and 2.6%, respectively.

Owing to the universal dynamics of organic cations in the metal-halide perovskites [130], each of the heterojunctions has a paraelectric configuration with randomly oriented organic cations. We optimise the ground-state geometries of these heterojunctions based on the DFT approach using the Vienna *ab initio* simulation package (VASP) [131] and employing the Perdew-Burke-Ernzerhof functional [132] in conjunction with the projector augmented-wave method [133]. The semi-empirical DFT-D2 method is used to account for the van der Waals corrections [134]. The cut-off energy used for the plane-wave basis set is 400 eV, and a k mesh with only  $\Gamma$  point is used during the geometry relaxation which has been shown to reasonably predict the bandgap for the metal-halide perovskites, with the sizes being comparable to the heterojunctions in this work [135]. The convergence criterions for total energies and forces are set to be 10<sup>-4</sup> eV and 0.04 eV/Å, respectively. The electronic excitation and excited-state geometric relaxation are obtained by employing a recently developed TDDFT approach in the framework of linear response theory [136], which calculates the charge densities and ionic forces of large-scale systems in the excited states, by the derivatives of the Lagrangian functional with respect to external potential and ionic position, respectively.

#### 3.7.2 Computational details for localisation studies in doped nanocrystals

In the following, the computational methods for the localisation study on doped nanocrystals in Chapter 5 is discussed. The modelling was carried out by Ivona Bravić and Bartomeu Monserrat.

# **3.7.2.1** General computational methods and parameters for localisation studies

We use first principles methods based on density functional theory [137,138] combined with the projector-augmented wave method (PAW) [133,139] as it is available in the Vienna *ab initio* simulation package (VASP) [131,140]. We use two different exchange correlation functionals, namely, the semilocal generalised gradient approximation of Perdew-Burke-Ernzerhof (PBE) revised for solids (PBEsol) [141,142] and the hybrid Heyd-Scuseria-Ernzerhof functional (HSE06) [143,144], albeit the latter is only used as a benchmark as well as for the 3.7 % Mn-doped CsPbCl<sub>3</sub> (Fig. 3c and d) due to a large computational expense. We employ PAW potentials containing nine valence electrons for Cs ( $5s^25p^66s^1$ ), fourteen valence electrons for Pb ( $5d^{10}6s^26p^2$ ), seven valence electrons for Cl ( $3s^23p^5$ ) and Br ( $4s^24p^5$ ), as well as thirteen valence electrons for Mn ( $3p^64s^23d^5$ ). Based on convergence tests we use a planewave basis set with an energy cutoff of 500 eV (pristine unit cells) and 250 eV (doped supercells) with a Brillouin-zone grid of  $6 \times 6 \times 6 \Gamma$ -centered k-points for the structural relaxation of the unit cell. We relax the cubic primitive cell for the single halide perovskites using the conjugate gradient algorithm until the energy differences are converged within  $10^{-6}$  eV, with a Hellman-Feyman force convergence threshold of 0.01 eV/Å.

For the single halide Mn-doped CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> we take the relaxed cubic primitive cells as reference structures to construct  $2\times2\times2$  and  $3\times3\times3$  supercells with uniform  $3\times3\times3$  and  $2\times2\times2$   $\Gamma$ -centered k-point grids, respectively. We replace a B-site Pb with a Mn and relax the structure using the conjugate gradient algorithm as stated above. For the mixed-halide systems we use a configuration below generated *via* the special quasi-random structure (SQS) method [145] and again replace a Pb atom with a Mn atom. Using DFT+U theory [146] we further test the dependence of the lattice parameters on different Hubbard parameters  $U_{eff} =$ U - J, and spin configurations within the Dudarev *et al.* formalism [147] as it is implemented in VASP [148,149]. A more detailed description for the geometry optimisations are found below.

# **3.7.2.2** Benchmark of U+J parameters for different ground-state spin configurations

A known drawback of DFT is the poor treatment of strongly correlated systems. GGA+U is one of the simplest approaches that was formulated to improve the description of the ground state of correlated systems and that is frequently used to circumvent the issue of predicting the magnetic ground state with a small computational expense [150]. For different  $U_{eff}$  we optimize the geometry for different spin configurations and find that the lattice parameters for nonmagnetic spin configurations decreases by ~1% with respect to the ferromagnetic spin alignment. The change in the lattice parameters for different  $U_{eff}$  remains negligible. For all  $U_{eff}$ , there was no preferred spin-configuration, suggesting that the ground state for a  $3\times3\times3$ supercell doped with a Mn atom (3.7%) has no preferred magnetic order. These observations

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hold true for all systems. The final structures are relaxed with a *U*-parameter of value 4 and a *J*-parameter of value 0.5 ( $U_{eff}$  = 3.5).

# **3.7.2.3** Benchmark of U+J parameters for correct band ordering in doped supercells

Another issue of DFT is the over-delocalization of *d*-states which falsely leads to overhybridization with the band edges of the system. This error can also be avoided by incorporating a U and J correction into the exchange correlation functional. Within the GGA+U formalism, the electrons of the system are separated into two subsystems. The first subsystem includes delocalized *s* and *p*-states, that can be described with the GGA. The second subset entails *d* electrons that require an additional on-site screened Coulomb potential. This Coulomb potential acts on the subset of *d* electrons and localizes the orbitals, mimicking the *d*-*d* repulsion. In contrast to that approach, hybrid functionals incorporate a portion of exact exchange in form of a Fock operator that acts on all Kohn-Sham states [150].

Albeit hybrid functionals have established themselves as the more accurate method, we do not use them for all systems because they are associated with a large computational cost. Therefore, we calculate the projected density of states for the Mn-doped  $2 \times 2 \times 2$  supercells of CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> using PBEsol with different U and J parameters as well as using the HSE06 functional with an energy cut-off of 250 eV and a  $3 \times 3 \times 3$   $\Gamma$ -centered k-point grid. We do not use the results for microscopic interpretations as we assume the doping concentrations to be too large to provide a realistic model system for low-concentration doping. We find that a U-parameter of 4 and a J -parameter of 0.5 ( $U_{eff}$  = 3.5) resemble the projected density of states obtained via the HSE06 functional the most. As expected, using HSE06 increases the bandgap for about 1 eV, while the band ordering is correctly captured by the  $U_{eff}$  = 3.5 value.

Hereafter we calculate the band structure and the projected density of states for the 3.7% doped CsPbBr<sub>3</sub>, CsPb(Cl,Br)<sub>3</sub> and CsPbBr<sub>3</sub> using the DFT +  $U_{eff}$  = 3.5 method with a 2×2×2  $\Gamma$ centered k-point grid. The projected density of states and folded band structures are depicted
in Fig. S7 and Fig. S8, respectively. While CsPbBr<sub>3</sub> and CsPb(Cl,Br)<sub>3</sub> prove particularly robust
with respect to the chosen Hubbard U parameters, the electronic structure of 3.7% doped
CsPbCl<sub>3</sub> appears much more sensitive due to the critical in-gap positions of Mn 3*d* states and

the somewhat poor description of Mn 4*s* states. Therefore, we also calculate the projected density of states at the HSE06 level of theory which is illustrated in the manuscript (Fig. 3d). Spin-orbit coupling is included throughout all electronic structure calculations using the second-variational method, in which the spin-orbit interaction is included perturbatively to the scalar-relativistic Hamiltonian [151].

# Chapter 4: Local Charge Carrier Accumulation in Alloyed Metal-Halide Perovskites for Highly Efficient Luminescence

Metal-halide perovskites have emerged as exceptional semiconductors for optoelectronic applications. Substitution of the monovalent cations has advanced luminescence yields and device efficiencies. In this chapter, we control the cation alloying to enhance optoelectronic performance through alteration of the charge carrier dynamics in mixed-halide perovskites. In contrast to single-halide perovskites, we find high luminescence yields for photo-excited carrier densities far below solar illumination conditions. Using time-resolved spectroscopy we show that the charge-carrier recombination regime changes from second to first order within the first tens of nanoseconds after excitation. Supported by microscale-mapping of the optical bandgap, electrically-gated transport measurements and first-principles calculations, we demonstrate that spatially-varying energetic disorder in the electronic states causes local charge accumulation, creating p- and n-type photo-doped regions, which unearths a strategy for efficient light emission at low charge-injection in solar cells and LEDs.

- This chapter is based on reference [152].

## 4.1 Background

Metal-halide perovskites exhibit outstanding optoelectronic properties, such as low Urbach energies, high carrier mobilities and diffusion lengths, as well as very high photoluminescence quantum efficiencies (PLQEs) [153], which are essential to achieve performance limits in solar cells and light-emitting diodes (LEDs) [56,57,88,154]. This culminated in reported

photovoltaic performances [155,156] exceeding 25% upon incorporation of a series of monovalent cation mixtures (formamidinium, Cs) and passivating additives (Rb, K) to the methylammonium mixed-halide perovskite prototype MAPb(Br<sub>0.17</sub>I<sub>0.83</sub>)<sub>3</sub> [67,157], as well as bright LEDs [100,158–162]. Here, we show that local bandgap variations in mixed-halide thin films yield photo-doped regions for efficient photoluminescence, favourable for optoelectronic applications.

## 4.2 Results

First, we find that external PLQEs for thin films of these configurations vary depending on composition, with values ranging from 2.7 - 40.9% champion performance from methylammonium lead bromide-iodide (MA) to potassium-passivated cesium methylammonium formamidinium lead bromide-iodide (KCsMAFA), respectively (Table 1).

Abbreviation	External PLQE (%)	Composition
MA-I	16.8±5	MAPbI <sub>3</sub>
MA	2.70±9	$MAPb(Br_{0.17}I_{0.83})_3$
MAFA	22.6±5	$MA_{0.2}FA_{0.8}Pb(Br_{0.17}I_{0.83})_3$
CsMAFA	21.6±5	$Cs_{0.05}(MA_{0.2}FA_{0.8})_{0.95}Pb(Br_{0.17}I_{0.83})_3$
RbCsMAFA	26.4±5	$Rb_{0.05} / Cs_{0.05}(MA_{0.2}FA_{0.8})_{0.95}Pb(Br_{0.17}I_{0.83})_{3}$
KCsMAFA	40.9±7	$K_{0.1} / Cs_{0.05}(MA_{0.2}FA_{0.8})_{0.95}Pb(Br_{0.17}I_{0.83})_{3}$

Table 1: Mixed-cation perovskite compositions investigated within this study. High external photoluminescence quantum efficiencies (PLQEs) were measured upon incorporation of a variety of monovalent cations and passivating additives to the mixed-halide prototype, using protocols reported in the literature [70,163,164]. Films were ~550 nm thick on glass substrates. Samples were excited using a continuous-wave diode laser with a photon energy of 2.38 eV at an excitation density equivalent to  $10^{15}$  cm<sup>-3</sup> (approx. solar illumination conditions, see Methods chapter for procedure details).

The PLQE data were taken under solar illumination intensities. We start our investigation on the origin of such significant efficiency differences by measuring the steady-state optical properties of the thin films (see Figure 31).



Figure 31: Steady-state optical absorbance (dotted lines) and photoluminescence (solid lines) spectra of thin films of the various perovskite compositions examined in this study.

We find similar optical properties with changing bandgaps for the different compositions, and furthermore similar light outcoupling conditions, as confirmed by comparable film morphologies from SEM micrographs (see Figure 32).



Figure 32: Scanning electron microscopy (SEM) images of (a) MA-I, (b) MA, (c) MAFA, (d) CsMAFA, (e) RbCsMAFA and (f) KCsMAFA samples. Scale bar is 1 µm. Images were provided by Michael Saliba.

Given that the steady-state characterisation is not sufficient to explain the performance observations made, we next investigate the charge carrier recombination processes underlying

these findings with transient photoluminescence (PL) spectroscopy to resolve how cation composition affects carrier population dynamics (Figure 33).



Figure 33: Transient photoluminescence (PL) kinetics of MAPb(Br<sub>0.17</sub>I<sub>0.83</sub>)<sub>3</sub> (MA) and MA<sub>0.2</sub>FA<sub>0.8</sub>Pb(Br<sub>0.17</sub>I<sub>0.83</sub>)<sub>3</sub> (MAFA) thin films with varying initial carrier density n<sub>0</sub>. Incorporation of FA cations leads to a significant increase in PL lifetime (36±1 ns for MA and 695±69 ns for MAFA at  $n_0 = 10^{16}$  cm<sup>-3</sup>, respectively). Inset: PL intensity as a function of initial carrier density for MAFA. Initially, PL scales quadratically with carrier density over a wide range of carrier densities, whereas at later times it scales linearly.

We find a large increase in lifetime of the PL kinetics upon incorporation of formamidinium (FA) into MAPb(Br<sub>0.17</sub>I<sub>0.83</sub>)<sub>3</sub> (yielding MAFA, for lifetimes of the other investigated compositions see Table 2), indicating a decrease in non-radiative losses. Plotting the initial PL intensity ( $PL_0$ ) against the initial excitation density ( $n_0$ ) (Figure 33, inset) yields a quadratic dependence over a wide range of carrier densities, as expected for a bimolecular radiative recombination of electrons and holes [165].

In Figure 34, we also confirm the expected trend of reduction in PL lifetimes with increasing excitation fluence as a result from the rate equation model established for perovskites described below.



Figure 34: Photoluminescence time constants as a function of initial carrier density  $(n_0)$ , for MA and MAFA samples, determined via monoexponential fits to the long-time delays where decay is dominated by Shockley-Read-Hall recombination. In MAFA, the radiative lifetime increases rapidly at low carrier density and remains high even at the largest  $n_0$ .

Next, we measure the dependence of PLQE on initial carrier density (Figure 35) and find that the values level out at high yield for low carrier densities.

Considering a general recombination rate equation model discussed in Chapter 2 of the form

$$-\frac{dn}{dt_{tot}} = a \cdot n + b \cdot n^2 + c \cdot n^3$$
(65)

describing the total rate of change of carrier density  $(dn/dt_{tot})$ , where *n* is the carrier density, *t* is time and *a*, *b* and *c* are recombination constants [88], the internal PLQE (*PLQE<sub>int</sub>*), given by the ratio of the radiative recombination rate  $(dn/dt_{rad})$  to the total recombination rate

$$PLQE_{int} = \frac{dn/dt_{rad}}{dn/dt_{tot}}$$
(66)

does *not* model the observed trends. The measured levelling out at low carrier densities is typical for doped semiconductors, and we find our results are accurately described on the inclusion of a doping term  $p_D$ , yielding:

$$PLQE_{int} = \frac{b (np + np_D)}{a (n + p + p_D) + b (np + np_D)}$$
(67)

The third order Auger term was excluded as its contribution is negligible for the investigated carrier density regime.



Figure 35: Fluence-dependent external PLQE measurements. PLQE values level out at low excitation densities for mixed-halide compositions, in line with a doping carrier density of  $\sim 10^{14}$  cm<sup>-3</sup>, while for MA-I the PLQE rapidly decreases.

This model is based on extensive studies of classical inorganic semiconductors like Si or GaAs, in which doping determines charge carrier recombination rates, initially based on work by Shockley, Read and Hall where the derivation of the above equation can be found in high detail [28,29]. This was then applied to hybrid perovskites by our group, as well as the groups of Herz, Beard and others [88,90,154,165–168]. All these studies are based on and give evidence for the model of a non-radiative monomolecular and radiative bimolecular recombination of free carriers, that provide the physical background of this work.

For a brief derivation, we start with the general rate equation and the relation of radiative to total recombination rates that describes the PLQE, leads upon excluding the third-order Auger term to:

$$PLQE_{int} = \frac{dn/dt_{rad}}{dn/dt_{tot}} = \frac{b n^2}{a n + b n^2}$$
(68)

If now the simple carrier density n is expanded to distinguish between electron (n) and hole (p) density, as well as a negative  $(n_D)$  and positive  $(p_D)$  doping density, the equation expands to

$$PLQE_{int} = \frac{dn/dt_{rad}}{dn/dt_{tot}} = \frac{b(n+n_D)(p+p_D)}{a(n+n_D+p+p_D) + b(n+n_D)(p+p_D)}$$
(69)

With significant hole doping and insignificant electron doping as we observe in this work and will be proven experimentally and theoretically further below, we can assume  $n > p_D \gg n_D$ , which includes  $n_D \ll n$ , and it follows:

$$PLQE_{int} = \frac{b n (p + p_D)}{a (n + p + p_D) + b n (p + p_D)}$$
(70)

which can be expanded to the form stated above. Using this expression, the trend of PLQE values levelling out at low excitation densities can be computationally modelled. As shown in Figure 36, the higher the doping density in the system is for a given general PLQE (i.e. ratio between radiative and all decay channels), the higher is also the resulting minimum PLQE value at low excitation conditions.



Figure 36: Influence of doping carrier density on fluence-dependent photoluminescence quantum efficiency (PLQE) behavior, as described by the modified rate equation model in the text. High doping densities lead to an increased base-levels of PLQE.

To shed light on the photo-induced doping effect in the perovskite films, we track the total carrier population dynamics with broadband transient absorption (TA) spectroscopy.

Figure 37 shows a typical broad-band TA data set of a perovskite thin film with a pronounced ground-state bleach (GSB) as a positive signal around 750 nm and a photo-induced absorption feature extending towards smaller wavelengths. While the GSB arises from the depletion of carriers in the valence band upon photo-excitation, thus allowing more probe light to be transmitted and detected, the high-energy feature has been assigned to a photo-induced refractive index change. A detailed discussion on this effect can be found e.g. by Price *et al.* in ref. [94]. All samples studied showed in principle the same spectral features with differences limited to the bandgap position and kinetics. Therefore, only the KCsMAFA 2D map is explicitly shown below as an example.



Figure 37: 2D pseudo-colour plot of transient absorption (TA) spectroscopy data, shown for a KCsMAFA sample as an example. The color scale shows the fractional change in sample transmission. The ground state bleach is observed as a positive feature, centered around 750 nm. A photoinduced absorption feature is present at higher energy.

In Figure 38a, the representative spectra from each film composition is shown at a pump-probe delay of 1 ns, where ultrafast processes like hot-carrier cooling are completed. The data is complementary to the initial steady-state absorbance and photoluminescence data shown above, reflecting on the different bandgap positions depending on perovskite composition. Moreover, in Figure 38b, we demonstrate the linear scaling of GSB intensity as a function of

excitation power over several orders of magnitude. This relationship allows us to indeed use the bleach signal as a probe for the carrier density in the sample upon excitation [88].



Figure 38: (a) Normalised TA spectra at 1 ns pump-probe delay. The addition of the FA<sup>+</sup> cation narrows the bandgap, causing a red-shift in the ground state bleach of the mixed-cation samples. Small dopant concentrations of CsI, RbI and KI have little effect on the bandgap thereafter. (b) Initial ground state bleach intensity scaling linearly with pump power. This relationship provides the conversion from bleach intensity to carrier density.

As set out by Richter *et al.* [88] in great detail, in Figure 39 we extract first-, second- and thirdorder rate constants for each composition from global fitting of the TA GSB data, knowing the initial carrier density  $n_0$ , which can be derived from excitation beam spot size, repetition rate, energy, and film absorbance. This estimation of initial carrier density has also been applied in all other instances where  $n_0$  is mentioned.



Figure 39: TA Ground-state bleach kinetics and global fits from the total carrier recombination rate dn/dt as a function of carrier density for different perovskite compositions: (a) MA, (b) MAFA, (c) CsMAFA, (d) RbCsMAFA, (e) KCsMAFA. Carrier dynamics for all compositions fit well to the rate equation in the text.

The extracted values for the recombination constants are displayed in Table 2. For comparison, we also include the monomolecular PL lifetime extracted from low-fluence PL kinetics, fitting a monoexponential after the initial intensity drop where the Shockley-Read-Hall regime holds. We will now discuss the observed trends in lifetimes in more detail.

Composition	<i>a</i> (s <sup>-1</sup> )	$b ({\rm cm}^3{\rm s}^{-1})$	$c ({\rm cm}^6{\rm s}^{-1})$	<i>a* (s<sup>-1</sup>)</i> from PL
MA-I	5x10 <sup>6</sup>	9.1x10 <sup>-11</sup>	1.1x10 <sup>-28</sup>	4.2x10 <sup>6</sup>
MA	(6.38±0.20)x10 <sup>6</sup>	(3.17±0.61)x10 <sup>-12</sup>	(2.08±0.26)x10 <sup>-30</sup>	3.1x10 <sup>7</sup>
MAFA	(1.98±0.07)x10 <sup>5</sup>	(7.27±0.26)x10 <sup>-12</sup>	(1.93±0.23)x10 <sup>-30</sup>	$< 3.4 \mathrm{x} 10^{6}$
CsMAFA	(3.46±0.17)x10 <sup>5</sup>	(5.29±0.30)x10 <sup>-12</sup>	(4.99±2.16)x10 <sup>-31</sup>	$< 4.8 \mathrm{x} 10^{6}$
RbCsMAFA	(1.50±0.04)x10 <sup>5</sup>	(6.27±0.37)x10 <sup>-13</sup>	(1.30±0.64)x10 <sup>-31</sup>	$< 3.0 \mathrm{x} 10^{6}$
KCsMAFA	(6.78±0.20)x10 <sup>5</sup>	(1.41±0.14)x10 <sup>-12</sup>	(2.06±1.35)x10 <sup>-31</sup>	2.3x10 <sup>6</sup>

Table 2: Rate constants (a, b, c) extracted from the fitted curves of carrier-density-dependent TA kinetics. MA-I parameters provided as a reference from the literature [88]. Films containing FA have reduced rate constants owing to their longer lifetimes. Monomolecular PL rate constants  $(a^*)$  were extracted via a mono-exponential fit of PL kinetics, excluding the initial intensity drop in mixed halide containing samples showing it.

For this, let us first compare directly the TA GSB kinetics with the PL kinetics in Figure 40. In the case of MA, both follow a similar decay at early times, before they eventually diverge at later times due to the bimolecular nature of PL recombination. By contrast, in MAFA (and all studied compositions containing FA), the PL does not follow the TA signal initially. Instead, there is an initial drop in PL signal, which indicates a decrease in radiative recombination rate, followed by a plateauing of PL intensity. The total carrier density in the material, reflected by TA, remains high. Still, much higher PLQE is observed in these films than in MA, suggesting an overall reduction in the impact of non-radiative recombination.



Figure 40: Tracking carrier recombination mechanisms with transient absorption (TA) and photoluminescence (PL) kinetics at an initial carrier density of  $n_0 = 10^{16}$  cm<sup>-3</sup>, where TA quantifies the total carrier density and PL only the radiative fraction. In the first 10 ns after excitation, a drop occurs in PL in the case of MAFA films which is not present in TA.

The MAPbI<sub>3</sub> (termed MA-I) sample – due to the absence of mixed halides – does not show such an initial drop. The divergence at later times in MA-I can be explained by the fact that TA kinetics decay proportional to the carrier density n(t),while PL kinetics decay proportional to  $n^2$ . In the mixed-halide MAFA, on the other hand, the PL signal undergoes an initial decrease followed by a plateauing which indicates the onset of the effective first-order radiative recombination due to a doping carrier density. The MAFA PL decay begins to track the TA signal (which directly maps out the carrier density) and does not diverge from it, indicating that the radiative recombination outcompetes non-radiative recombination due to a photodoping effect, as becomes clear from the effective first-order dependence of PL on carrier density in the following.

In Figure 41 we first confirm for MAPbI<sub>3</sub> (MA-I) the reported second-order dependence [88] of PL on total carrier density  $(n_{total})$ , the latter being extracted from our TA kinetics using time as an implicit variable.


Figure 41: Dependence of PL intensity on total carrier density. For this, the time-dependence of the PL kinetics was transformed into a carrier-density-dependence using the total carrier density that was derived from TA measurements by setting time as an implicit variable. While MA-I shows a quadratic PL-dependence [88] on carrier density, first-order recombination behaviour is observed in compositions with mixed halides, resulting in high brightness at low carrier densities. We note that the highly efficient PL of mixed-halide MAFA and RbCsMAFA decayed too slowly to be mapped over carrier densities as low as for the faster decaying MA-I (due to second-order dependence) or mixed-halide MA (due to more non-radiative losses).

Surprisingly, the addition of a small fraction of bromide anions in mixed-halide MA films leads to the change from second- to first-order dependence of PL on total carrier density, the timescale of which is linked to the initial PL drop, occurring within 10 ns after photo-excitation, as displayed in Figure 40. While the introduction of mixed halides in MA samples does change the recombination mechanism from bimolecular to monomolecular, the corresponding PLQE remains low. This indicates strong non-radiative losses due to higher defect densities than MA-I, explaining why an initial drop in PL similar to mixed-halide MAFA in Figure 40 cannot be resolved in this case. However, PLQE increases upon addition of FA. For these MAFA mixedhalide films, the PL signal decays proportional to n, while for MA-I PL decays with  $n^2$ . This leads to the relative PL intensity of mixed-halide MAFA remaining ca. ten times higher than for MA-I under low carrier densities comparable to solar illumination conditions (carrier density  $\sim 10^{15}$  cm<sup>-3</sup>). The reasons discussed in literature for the better performance of FAcontaining films include the suppressed ion migration compared to MA-only [169] and

increased crystallinity through reduction of defect states in the bulk for MAFA [170–172]. FA cations stabilise the unexpected, beneficial change to first order dependence of PL introduced by the mixed halides, to ultimately harvest this photo-doping effect for high PLQEs. Adding Cs, Rb or K cations to the alloy continues to reduce non-radiative losses. The reported origins of these reduced losses include the reduction of defect states in the bulk lattice for Cs [163,173] and Rb [173,174], as well as surface passivation for K [164], or stabilisation of the crystal structure against lattice strain, also reducing non-radiative losses [175] – without changing the underlying recombination mechanism which remains effectively first order for all mixed-halide films.

We stress that this quasi-first-order dependence should not be confused with the first-order non-radiative rate constant in the overall evolution of carrier population, given by Eq. 65. In the latter, the recombination rate is dominated by the first-order non-radiative term at carrier densities low enough for the majority of charges to be trapped by defects (surface *and* bulk), yielding  $-dn/dt \approx a \cdot n$ . Low carrier densities thus decay dominantly with  $n(t) = n_0 \cdot e^{-at}$ , while PL kinetics in this regime are described by:

$$PL(t) \sim b \cdot n^2 = b \cdot n_0^2 \cdot e^{-2at} \tag{71}$$

The PL will show a mono-exponential decay, while the underlying recombination mechanism remains bimolecular and depends quadratically on the carrier density. In Figure 40 we plot the kinetics of PL intensity and TA ground-state-bleach intensity, which is a measure for n(t), and we find that at low carrier densities the PL of MA-I decays by a factor 2 faster than the TA signal, as expected from the above formulism. The combination of both TA *and* PL experiments is essential to provide detailed insights into the recombination mechanism, which is not possible from PL kinetics alone.

The origin of the first order recombination and photodoping implied by the fluence-dependent PLQE series can arise from one charge carrier type accumulating locally in large excess due to heterogeneity in the energy landscape, creating n/p-type regions of the film. To test the above hypothesis, we perform temperature-dependent PL measurements (Figure 42).

We find that the PL of mixed-halide MAFA overall increases and the peak red-shifts with decreasing temperature (Figure 42, inset), in line with earlier observations on related perovskite compounds [176]. The improved phase stability of FA-based mixed-halide compositions [177,178] enables us to compare the kinetics of the low-energy and high-energy regions of the PL spectrum at different temperatures (Figure 42).



Figure 42: Temperature-dependent luminescence of mixed-halide MAFA films. (a) PL kinetics, spectrally integrated over high-energy region, 720 - 730 nm, and (b) low-energy region, 785 - 795 nm. At 300 K, both sides of the PL spectrum show similar kinetics, whereas at 100 K the high-energy part decays faster than its low-energy counterpart. Inset: Area-normalised temperature-dependent PL spectra. The arrow indicates a 4-fold increase in integrated PL over 720 - 730 nm (dotted lines). The measurements were performed at an initial carrier density of  $n_0 = 10^{16}$  cm<sup>-3</sup>.

We find comparable kinetics in the low-energy region, but a drop in PL intensity for lower temperatures in the high-energy region – an observation that is highly unlikely to be explained by phonon-interactions, since phonon-absorption is much less likely than phonon-emission upon photoexcitation, which we do not observe [179]. High-energy sites quickly become less populated at lower temperatures. These results strongly point towards energetic disorder in the film, which will localise charges in regions of local energy minima (Figure 43).



Figure 43: Scheme illustrating a model for energetic disorder in the energy levels of mixed-halide perovskite films. This leads to spatial accumulation of one carrier type, invoking strong local doping. Thereby, radiative charge carrier recombination is diffusion-limited by the more mobile carrier type, and hence effectively monomolecular.

Accumulation of electrons and holes in different regions of the film will then create local excess of one carrier species, with an energy barrier hindering them from returning to high-energy sites. The emission rate in these regions only depends on the density of minority carriers (the opposite charge density being dominated by the doping-induced density) – hence we observe first-order recombination. We note that these findings are different from reports on shallow traps [180,181], since such traps would ultimately result in increased fractions of non-radiative recombination and thus not lead to the observed increase in PL performance.

The PL peak energy map displayed in Figure 44 confirms these different energy sites and shows a heterogeneous distribution of local domains.



Figure 44: Confocal microscopy PL mapping of different domains in an MAFA mixed-halide film. The regiondependent PL peak energy difference is on the same order of magnitude as the measured activation energy, as described in the main text. Scalebar is 5 µm.

We estimate the carrier transport length to these sites (*L*), using a diffusion-like model  $L = \sqrt{D\Delta t}$  by considering reported diffusion constants ( $D = 1.09 \text{ cm}^{-2} \text{ s}^{-1}$  for MAFA) [182,183] and the timescale,  $\Delta t$ , of the initial PL drop in Figure 40 (ca. 10 ns for mixed-halide MAFA) – the time taken for carriers to localise in low energy regions and display first-order PL kinetics. Transport lengths on the order of ~  $1.0 \pm 0.5 \mu m$  are in accordance with domain sizes in the PL map (Figure 44). Further, the PL peak energy difference between different spatial regions is on the order of tens of milli-electronvolts, matching activation energies for carriers found from an Arrhenius-like plot for the temperature-activated PL lifetime as a rough estimate (see Figure 45).



Figure 45: Arrhenius-like plot of high energy kinetics, shown for the example of mixed-halide MAFA film from Figure 42, where *a* is the rate constant of the PL decay at sample temperature *T*. The slope yields a deactivation energy of  $(31 \pm 3)$  meV for carrier localisation.

While typical grain sizes are on the order of few hundred nanometres (e.g.  $\sim 200$  nm for mixedhalide MAFA, Figure 32), typical PL energy domain sizes cover several microns (e.g.  $\sim 2-5$  µm for mixed-halide MAFA). This provides further evidence that sample morphology alone cannot be the origin of our observed photo-doping. MA-I, with a very similar SEM profile does not show the same PL energy variation (Figure 46), providing strong evidence that the variation of iodide and bromide content is key.



Figure 46: Confocal PL microscopy maps of (a) MA-I and (b) mixed-halide MA films, showing contrasting degrees of energy heterogeneity. MA-I has an extremely uniform PL peak energy distribution owing to the presence of only iodide anions. As with mixed-halide MAFA, the mixed-halide MA film displays energy non-uniformity on the micron-scale with variations of  $\sim$ 30 meV in PL peak energy. Scalebar is 5 µm.

Compositional mapping using electron probe microanalysis (EPMA) shows I- and Br-rich regions with similar size as in our PL maps (Figure 47).



Figure 47: Electron probe microanalyser (EPMA) map for a mixed-halide CsMAFA sample, mapping the ratio of iodine  $L_{\alpha}$  emission to total halide emission (iodine  $L_{\alpha}$  + bromine  $L_{\alpha}$ ). Significant compositional heterogeneity is observed along with evidence of iodine-rich regions. Scalebar is 5 µm. EPMA data were taken by Tiarnan Doherty, Iris Buisman and Emilie Ringe.

These results, measured in the dark without exposing the samples to light, suggest the compositional heterogeneity is a consequence of an initial chemical distribution upon film formation, rather than light-induced halide segregation, which is common for less stable mixed-halide films than used here [75,184].

Our observation of increased PL yields from localised charge carrier accumulation has significance for the efficiency of both solar cells and LEDs. The observed charge accumulation regions are on the micrometre-scale, laterally. With film thicknesses  $<1 \mu m$  it is likely that channels of the low-bandgap composition are present between the top and bottom surfaces, in which photo-excited carrier densities remain high, above the trap-limited regime. This leads to the desired scenario of dominant radiative recombination at device-relevant (i.e. low) carrier densities. In LEDs, these channels are likely to act as efficient emitter regions for high electroluminescence efficiency at low carrier injection, while in solar cells they are a pathway of improved transport, reduced non-radiative losses and improved photon recycling [56] for efficient charge extraction and high open circuit voltage in low light conditions [185]. For these reasons, charge carrier doping has been important for a wide range of breakthroughs in current

commercial semiconductor systems, such as GaAs which is a world-leading PV technology, with performance approaching the radiative limit [158,164,186]. We now find that charge carrier doping occurs intrinsically under illumination in the crudely processed perovskite thin film semiconductors. We probe the nature of the localised charge carriers and the extent of photodoping with field-effect transistor (FET) measurements on bottom-gate bottom-contact FETs in the dark and under illumination, as set out in Figure 48.



Figure 48: Electrically-gated measurements of charge transport in perovskite devices of varying composition. The transfer characteristics of the FETs ( $L = 100 \mu m$ , W = 1 mm) with drain voltage ( $V_d$ ) fixed at 60 V also vary for different excitation densities ranging between dark, 0.05 and 0.1 sun (white light illumination). The arrows in (a) indicate the direction of measurements with increasing illumination (black) and scan direction (blue), respectively, as applying to the compositions shown in (b)-(e). Transistors were fabricated by Satyaprasad Senanayak.

In the fabricated bottom-gated Si/SiO<sub>2</sub>-based FETs, charge transport occurs at the SiO<sub>2</sub>/perovskite interface. When  $V_g > 0$  (or  $V_g < 0$ ) is applied, electrons (or holes) are induced at the interface, which results in a channel current under suitable drain bias. Hence, n-type semiconductor devices exhibit gate modulation when  $V_g > 0$  and a p-type semiconductor exhibits gate modulation in  $V_g < 0$  regime. Correspondingly, ambipolar semiconductors exhibit gate modulation in both the positive and negative  $V_g$ . All perovskite FETs shown in this study exhibit gate modulation for  $V_g > 0$ , indicating n-type transport. It should be noted that demonstration of gate modulation in perovskite thin films at room temperature has been difficult due to ionic screening of the gate modulation. Nevertheless, it is worth pointing out that the gate modulation shown here is comparable to most reported state-of-art perovskite thin-film transistors (e.g. in refs. [187,188]).

Upon illumination, electrons and holes are induced at the interface which increases the bulk conductivity of the sample. Hence, there is a decrease in the gate modulation of the sample. This is reflected by a decrease in ON/OFF ratio from 60 to around 4 for the MAFA-based mixed-halide composition. In comparison, FET devices fabricated with single-halide MAPbI<sub>3</sub> (MA-I) exhibit only a rather small decrease of ON/OFF ratio from 60 under dark condition to 40 under illumination. Consistently, the photo-induced charge density estimation indicates ease of photodoping for samples fabricated with MAFA mixed-halide compositions compared to conventional single-halide MAPbI<sub>3</sub>.

While these results on their own cannot fully exclude a contribution to the observed changes as a consequence of halide migration – a commonly assigned origin for the observed hysteresis in perovskite-based devices – together with all previously shown results from other experiments in this study, they strongly support the argument of charge accumulation as a consequence of the heterogeneous energy landscape set out by the varying halide-ratios across these materials, which we here propose.

The transfer characteristics measured at room temperature in the dark and under illumination show loss of gate modulation at negative voltages, thereby confirming localisation of *holes*, indicating excess localised p-type carriers, while electrons remain mobile and cannot be fully depleted. A strong increase in photo-induced carrier density, extracted from the capacitance, threshold voltage and maximum gate voltage, is observed for films containing FA cations (Figure 49).



Figure 49: Photo-induced charge density in perovskite thin-film field-effect transistors. Notably, only in presence of both MA and FA cations is a substantial increase in photo-induced charge density observed. The applied excitation density is normalised to 0.1 sun. Transistors were fabricated by Satyaprasad Senanayak.

We take this as further validation of our spectroscopic observation that MA and FA ions must be present together to stabilise doping of higher carrier concentration in the mixed-halide perovskites. Potentially, FA ions facilitate a larger phase separation between bromide and iodide regions to allow for more stable charge accumulation or passivate the interface between these regions to reduce losses when carriers cross between them.

Finally, we perform density functional theory (DFT) and time-dependent DFT (TDDFT) calculations to model the Br-I and the MA-FA heterojunction in mixed-halide films, respectively (Figure 50).



Figure 50: DFT- and TDDFT-calculations reveal driving force for mixed-halide mediated charge separation. (a) Charge densities of the lowest excited-state geometry relaxed from the optimised ground-state geometry of MAPbI<sub>3</sub>/MAPbBr<sub>3</sub> heterojunction along the *a* axis, showing charge localisation across the Br – I heterojunction. (b) Charge densities of the lowest excited-state geometry relaxed from the optimised ground-state geometry of FAPbI<sub>3</sub>/MAPbI<sub>3</sub> heterojunction along *a* axis, displaying no additional driving force for charge segregation across the MA–FA interface. (c) Charge densities of the lowest excited state for the optimised ground-state geometry of MAPbBr<sub>3</sub>/FAPbI<sub>3</sub> heterojunction. The ground-state energy is 28.3 meV nm<sup>-3</sup> smaller than the one for the MAPbI<sub>3</sub>/FAPbBr<sub>3</sub> heterojunction indicating matched ion radii stabilise charge separation across the lattice. The electron (hole) density is shown in red (yellow) in (a), (b) and (c); the value of isosurface is  $1.5 \cdot 10^{-3}$  e Å<sup>-3</sup> in (a) and (c), and  $7.0 \cdot 10^{-4}$  e Å<sup>-3</sup> in (b). Modelling was performed by Guangjun Nan and David Beljonne.

These reveal a driving force for confining holes in iodide-rich and electrons in bromide-rich domains, though we stress that charge carriers can still visit both regions, as seen in the excited-state density distributions (Figure 50a). This observation is in line with previously reported energy off-sets between bromide- and iodide-based perovskites [189,190]. The calculations further indicate that at the MA-FA heterojunction no intrinsic driving force for charge separation is induced (Figure 50b), suggesting predominantly lattice-stabilisation rather than an electronic influence. Lastly, Figure 50c shows that matching the smaller MA ion with

bromide and the larger FA ion with iodide reduces the energy of the system by almost 30 meV nm<sup>-3</sup> while maintaining charge separation across the heterojunction as opposed to an ion radius mismatch.

## 4.3 Conclusions

Our results have profound implications for solar cells and LEDs, in which efficient luminescence at low carrier densities is required for high performance. Charge confinement and energy gradients in 2D/3D perovskite LEDs have so far been exploited to boost radiative efficiency [100,191,192] but require complex device engineering. Here, we find that mixedhalide perovskites form self-organised bandgap gradients, leading to charge accumulation in local low-bandgap regions - an effect which is stabilised by a tailored selection of cations. Our observation of exceptionally high levels of PLQEs at excitation densities below solar flux demonstrates a novel strategy for scalable, high-efficiency LEDs. For this, transfer rates into the accumulation regions and localisation potentials can be tailored by chemical postdeposition treatments [193], precise control over spatial halide patterns from scalable phase self-organisation [194], evaporation [195] and lithography [196–198] on the microscale to drive radiative yields towards their fundamental limits. In contrast to previously reported irreversible trapping of carriers in deep trap-states, which has been argued to slow down nonradiative recombination [199], our observed photo-doping leads to charge separation and accumulation within a disordered landscape of bandgaps. The observed increases in luminescence yields originate from radiative rates outcompeting non-radiative losses, since carrier densities remain locally high in these charge-accumulation regions. While decoupling of the detailed distribution of emission sites and the relative contributions of bulk and surface recombination is beyond the scope of the current study, future efficiency gains are expected from addressing these questions and controlling the effect to maximise performance in LEDs and solar cells. In summary, we report a change from second to first order charge-carrier recombination in mixed-cation perovskites due to localised, photo-doped regions - moving perovskite materials closer to semiconductors like GaAs or GaN, where doping unlocked their full potential for optoelectronic technologies [200-203]. Our findings contribute to the understanding of the excellent performance of alloyed perovskite optoelectronics to date and, importantly, highlight the potential for perovskites to approach the performance of GaAs photovoltaics and optoelectronics.

## Chapter 5: Manganese Doping of Perovskite Nanocrystals Localises Charge Carriers for Bright Emission

Nanocrystals based on halide perovskites offer a promising material platform for highly efficient lighting. Using transient optical spectroscopy, we study excitation recombination dynamics in manganese-doped CsPb(Cl,Br)<sub>3</sub> perovskite nanocrystals. We find an increase in the intrinsic excitonic radiative recombination rate upon doping, which is typically a challenging material property to tailor. Supported by *ab initio* calculations, we can attribute the enhanced emission rates to increased charge carrier localisation through lattice periodicity breaking from Mn dopants, which increases the overlap of electron and hole wavefunctions locally and thus the oscillator strength of excitons in their vicinity. Our report of a fundamental strategy for improving luminescence efficiencies in perovskite nanocrystals will be valuable for maximising efficiencies in light-emitting applications such as light-emitting diodes, as well as for quantum emitters and lasing devices, where high radiative rates are desirable.

- This chapter is based on reference [204].

## 5.1 Background

Metal-halide perovskite nanocrystals (NCs) have been the subject of intense investigation due to their high brightness, spectral tunability and excellent color gamut, making them ideal candidates for low-cost and highly efficient light-emitting diodes (LEDs) [102,105,205]. Recently, doping of these NCs with manganese ions has resulted in increased efficiencies in perovskite-based LEDs [110].

Doping of traditional II-VI, II-V, and group-IV nanocrystal semiconductors was shown to successfully modify electronic, optical and magnetic properties [206–208]. Here, intentionally introduced impurities with more/less valence electrons than the host atoms can lead to increased conductivity through n-/p-type doping, while magnetic dopants could show increased interactions between carriers and spins due to the confinement within the NC, promising for

spintronic devices [209]. So far, efforts to utilise dopants for achieving exciton localisation have been limited to protecting materials against photo-oxidation by suppressing degradation reactions at the NC surface under prolonged illumination, *e.g.* in solar cells [210]. In these systems, efficient energy transfer to the dopant results in complete quenching of the host exciton emission. Alternatively, attempts to exploit exciton localization to increase emission rates rely on core-shell architectures for wave function engineering [211,212], which are synthetically challenging [213].

Using transient optical spectroscopy and *ab initio* calculations, here we report that manganese doping in perovskite NCs results in an increase in radiative exciton recombination rate, which we attribute to an increased degree of exciton localisation and concomitant overlap of electron and hole wave functions. Our results present a fundamental mechanism of how transition-metal doping in perovskites impacts band structure and excitonic properties of metal-halide perovskite nanocrystals, and provide a new concept for application in high-performance LEDs, as well as related fields like photocatalysis.

## 5.2 Results

We first characterise the synthesised Mn-doped CsPb(Cl,Br)<sub>3</sub> perovskite NCs with regard to their structural and optical properties (see Methods Chapter for synthesis according to reported protocols [110]). We employ transmission electron microscopy (TEM) and confirm a cubic structure of the NCs with a lattice spacing of about 0.5 nm and an average NC size of approximately 12 nm, as shown in Figure 51.

Similar sizes are found for all undoped and manganese-doped crystals studied here. This allows us to compare the impact of Mn-doping on optoelectronic properties quantitatively, excluding effects related to dielectric screening and quantum confinement that might arise from different crystal shapes or sizes [37,214,215].



Figure 51: Transmission electron microscopy image of doped NCs (shown exemplary for 1.9 atomic ‰ Mn:Pb) with cubic morphology and an average crystal size of 12±2 nm. Scale bar is 10 nm. Image taken by Mahesh Gangishetty.

We further take X-ray diffraction data (Figure 52) on undoped NC films and those doped with 1.9‰ Mn:Pb atomic ratio, as determined by inductively-coupled plasma mass-spectrometry (ICPMS).

We find very similar diffraction peak patterns across all compositions, with the peaks shifting to higher angles with increasing Mn-doping, as reported before [109,216,217]. This relates to a moderate degree of lattice contraction which is expected from the incorporation of the smaller manganese(II) ion (1.4 Å) substituting the larger lead(II) ion (1.8 Å) in the octahedral halide coordination sphere.



Figure 52: X-ray diffractogram of undoped (black) and 1.9‰-Mn doped (purple) nanocrystals, respectively. While (a) shows a larger range of diffraction angles, (b) focusses on the peak around 30.5° showing a slight lattice contraction upon doping. XRD data taken by Mahesh Gangishetty.

In the steady-state absorption and photoluminescence (PL) spectra (Figure 53) we observe a gradual blue-shift in both absorption and emission with increasing doping level, ranging from 0 to 2.5%, consistent with previous reports on manganese-doped perovskite NCs [109,217,218].



Figure 53: Steady-state absorbance (bold lines) and photoluminescence (PL, filled) of NC solutions for increasing Mn-doping, showing a doping-induced blue-shift of the excitonic transition around 2.7 eV. Samples were photoexcited with 3.1 eV pulsed excitation at a fluence of 127  $\mu$ W cm<sup>-2</sup>. The spin-forbidden manganese *d-d* transition around 2.1 eV is absent in the absorption spectra and only emerges in PL at our highest doping level.

All compositions show an excitonic peak close to the absorption onset. Notably, while all samples exhibit an intense blue excitonic emission (X) at around 2.7 eV, only the most doped 2.5‰ sample shows a low-intensity broad orange emission centred at 2.1 eV. This spectral feature is the well-known manganese(II)  ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$  (*d-d*) transition. Due to its spin- and parity-forbidden nature, this transition is not detected in our absorbance spectra, and its weak PL intensity reflects on its low oscillator strength. This is further confirmed by the long emission lifetime on the order of tens of microseconds (compare Figure 55, which will be discussed in detail further below). Most notably, the excitonic emission intensity increases by

a factor of 3.3 from 0 to 1.9‰ manganese doping, and then drops again for the 2.5‰ sample (see Figure 54).



Figure 54: Absolute photoluminescence spectra of nanocrystals with varying composition (inset: PL maxima as a function of doping level with the strongest PL achieved at 1.9‰ Mn).

This finding is important for optimising colour-pure blue light-emitting diode (LED) efficiencies – a wavelength regime in which it is particularly hard to achieve high efficiencies [219–223]. Our results are in contrast to the emission of Mn-doped perovskite NCs reported previously [109,217,218,224], in which the excitonic emission remained mostly unchanged or decreased upon Mn doping. In those studies, the manganese doping levels are often on the order of percent [109,216,217,225,226] and in consequence the manganese emission competes with similar or even higher intensity with the excitonic emission. The doping levels we employ here are an order of magnitude lower than those reported systems, which directly translates into a cheaper manufacturing route to these optimised devices. In the following we will investigate why the efficiency of the excitonic emission increases.

For this, we first determine the total exciton decay lifetime from time-resolved PL (Figure 55).



Figure 55: Time-resolved photoluminescence decay of (a) the excitonic emission at approximately  $10^{-5}$  excitations per nanocrystal. Triexponential fits yield the highest average PL lifetime  $\langle \tau_X \rangle$  for the 1.9‰ doping level. (b) Longlived manganese emission from the sample with highest doping level. We note that the extracted lifetime is underestimated, since it was not possible to measure with longer time delays than 50 µs at our setup. All measurements taken at 400 nm excitation using time-correlated single-photon counting (TCSPC).

By employing low-fluence time-resolved single-photon counting experiments we find that the 1.9‰ composition exhibits the longest average PL lifetime. We also find that the PL kinetics for all compositions can only be fitted to a high satisfying level if not less than the sum of three exponentials is used according to:

$$PL(t) = \sum_{i=1}^{n} a_i e^{-t/\tau_X^i}$$
(72)

with  $\tau_X^i$  as effective single-exciton lifetime (including both radiative and nonradiative contributions) and  $a_i$  the relative fraction (in sum being 1) of NCs in the *i*-th out of *n* subensembles possessing this lifetime. The necessity of a triexponential fit is in line with other reports on similar perovskite nanocrystals, for example by the groups of Klimov [215] or Herz [227]. As described in the references, we assume all nanocrystals measured in the ensemble to possess the same radiative recombination constant  $k_{r,X}$ , which is the inverse of the intrinsic radiative lifetime  $\langle \tau_{r,X} \rangle$ , while the nonradiative recombination constant  $k_{nr,X}$  can differ for sub-ensembles, e.g. due to different trap densities or identities. From weighting the individual sub-ensemble lifetimes via  $a_i$ , we can determine the average PL lifetime  $\langle \tau_X \rangle$  and hence the average total recombination constant  $\langle k_X \rangle = \langle \tau_X \rangle^{-1}$ . The photoluminescence quantum efficiency (PLQE) of each sub-ensemble is then the ratio of its radiative to total recombination rate, and the total PLQE of the ensemble therefore:

$$PLQE = \frac{\langle \tau_X \rangle}{\langle \tau_r \rangle}$$
(73)

From measuring PLQE and total PL lifetimes, the intrinsic radiative lifetime and hence recombination constant can be determined. Furthermore, the average non-radiative recombination rate can be calculated, since

$$k_{nr,X} = \langle k_X \rangle - k_{r,X} \tag{74}$$

In Figure 56, we then quantify the positive impact of the Mn-doping on the emission properties PLQE measurements.



Figure 56: Photoluminescence quantum efficiency (PLQE) as function of manganese doping for the perovskite excitonic (X) and Mn (d-d) emission with a maximum for 1.9‰ Mn-doping.

We find that the PLQE of the excitonic emission increases by a factor of 2.2 upon Mn doping up to 1.9% manganese, reaching values close to 40%. For the highest doping level of 2.5%, the PLQE of the excitonic emission decreases again, while the Mn *d-d* emission becomes detectable. This suggests the existence of a threshold doping level between 1.9 and 2.5‰, upon which energy transfer from the perovskite host exciton to the dopant becomes significant.

We note that, in contrast to the PL measurements shown in Figure 53 and Figure 54 which were integrated over a nanosecond time window upon photoexcitation, the PLQE measurements shown here are fully time-integrated. Thus, in the PLQE measurements the d-d

emission's relative intensity appears larger compared to the only small fraction of light detected from the slow emission process in the experiments discussed above.

Next, we investigate the fluence-dependence of the luminescence (Figure 57).



Figure 57: Fluence-dependence of spectrally integrated PL intensity over exciton and Mn emission, respectively. Solid lines are power-law fits of  $P^m$  with excitation power P and slope m indicated in the figure panel. All series exhibit linear dependence, indicating excitonic emission. Samples were photoexcited with 3.1 eV pulses.

We find that the photoluminescence of the excitonic emission of all compositions investigated, as well as the *d-d* emission displayed by the highest doping concentration, scale linear over the studied range of excitation fluences. This indicates that the time-integrated emission is dominated by single-exciton recombination even in the case of high excitation levels for which several excitons are generated initially in a NC [37]. The excitonic behaviour agrees with the pronounced excitonic absorption peak and weak quantum confinement [37] of excitons with predicted Bohr radius of about 2 nm in our NCs with size of about 12 nm. With a unit cell volume of approximately 200 Å<sup>3</sup> (in agreement from DFT- and XRD-based results) and a nanocrystal volume of about  $8 \times 10^{-24}$  m<sup>3</sup> from our STEM measurements, we find an average density of ~40 – 100 Mn dopants per NC for a doping concentration of 1 - 2.5%. Assuming cube-shaped nanocrystals, the mean spacing between Mn dopants is thus ~6 – 4 nm, for the given range of doping concentrations. In contrast, the exciton diffusion lengths reported

for cesium lead halide nanocrystals vary between 30 nm and 200 nm (see e.g. ref. [228] for a recent literature overview). Therefore, we conclude that an exciton generated in a nanocrystal will experience the presence of a manganese dopant, and we will discuss the nature and consequences of these interactions later on.

Combining PLQE and TCPSC results, we can extract the radiative and non-radiative recombination rates of all compositions, as shown in Figure 58 and also listed in Table 3.



Figure 58: Dependence of radiative and non-radiative recombination rates on Mn doping, showing a continuous increase in radiative rate and a minimum in non-radiative rate at 1.9‰ Mn doping. Samples were photoexcited with 3.1 eV pulses (repetition rate 1 kHz, pulse duration ~100 fs).

The non-radiative rate, which represents loss channels for luminescence, decreases upon Mndoping, reaching its minimum for the composition with the highest PLQE.

The initial decrease in non-radiative rate we observe at low doping concentrations is likely a consequence of the added MnCl<sub>2</sub> filling the pre-existing halide vacancies, thus reducing the trap density and with it the non-radiative rate. We assign the observed minimum in non-radiative rate at 1.9‰ Mn doping concentration to the limit after which Mn cluster formation takes place. Those clusters have been reported in previous reports on systems with high doping levels, and can be also reproduced by Monte Carlo simulations [229]. The Mn<sub>x</sub> clusters are not

structurally compatible with the perovskite crystal lattice and therefore act as defect sites, subsequently enhancing the non-radiative rate. This argument is further supported by the onset of the observable d-d emission at this concentration, for which the Mn d orbitals in those clusters start to hybridize and form the observable new energy band (which they could not form as separated dopants dispersed in the NC). This is evidenced by both our DFT simulations below, and the observed orange emission at high doping densities in our PL spectra above.

Mn-doping concentration (atom‰)	$\langle k_X \rangle  (10^7  \mathrm{s}^{-1})$	PLQE (%)	$k_{r,X} (10^7  \mathrm{s}^{-1})$	$k_{nr,X} (10^7  \mathrm{s}^{-1})$
0	8.48	17.7±6	1.50	6.99
1.0	8.26	21.7±6	1.79	6.49
1.9	4.90	38.4±6	1.88	3.02
2.5	9.90	25.0±6	2.48	7.41

Table 3: Manganese-doping simultaneously enhances radiative and decreases non-radiative recombination. The inverse of the average PL lifetime as determined from TCPSC  $\langle k_X \rangle$  and the non-radiative recombination constant  $k_{nr,X}$  are minimal for the 1.9‰ doping level, while the PLQE is here maximal. The radiative recombination constant  $k_{r,X}$  continues to further increase with higher doping concentration. Measurements taken at 400 nm excitation at a low-energy flux of 127  $\mu$ W cm<sup>-2</sup>.

Notably, we further find that the radiative recombination rate increases with doping level, leading to the highest radiative rate of  $2.5 \times 10^7$  s<sup>-1</sup> for the 2.5‰ doping. This increase in the radiative recombination rate, which relates to intrinsic properties of a material, indicates that the manganese dopants alter in fact the exciton dynamics and electronic structure in the perovskite host fundamentally. While the decrease in non-radiative rate observed here and reported before (e.g. in refs. [110,230]) follows optimisation strategies on trap-passivation in halide-perovskites and semiconductors generally (see e.g. [231]), it is the increase in radiative rate through doping that represents a fundamentally novel finding in our systems. Even though the PLQE gains from non-radiative rate increases, it is the latter observation that provides a novel route to enhance future material performance, since the discovered doping-induced localisation would improve radiative rates even in materials which have reached zero non-radiative losses, beneficial for lasing and quantum emission.

Next, we take transient absorption (TA) data in order to unveil all possible excitation decay channels, both radiative and non-radiative in nature. All compositions displayed similar spectral features and an exemplary 2D plot is presented in Figure 59, showing an expected ground-state bleach (GSB) around 450 nm and photo-induced absorption around 460 nm (see previous chapters for a more detailed discussion).



Figure 59: 2D pseudo-colour plot of exemplary long-time TA data, here shown for the 1.9‰ doping level at approx. 1.1 initial average excitations per NC and 3.5 eV pulsed excitation.

To identify the fundamental origin of the increased radiative recombination rates, we track the time-dependent excited-state dynamics by comparing kinetics obtained from the excitonic PL and the GSB kinetics of transient absorption under the same excitation conditions, and compare them directly (Figure 60).



Figure 60: Charge carrier dynamics in manganese-doped perovskite nanocrystals, with transient photoluminescence (PL) and transient absorption (TA) ground-state bleach (GSB) kinetics, showing similar lifetimes in TA for all compositions, while PL initially remains higher for doped samples. Monoexponential kinetics are observed for time delays beyond 200 ns for all compositions with a shared lifetime of  $116\pm 2$  ns (red line). PL and TA signals were spectrally integrated over the respective peak maximum; initial excitation density approx. 1.1 excitations per NC on average. Samples were photoexcited with 3.1 eV pulses.

Both techniques (TA and PL) probe the decay of photo-generated excitons. TA kinetics probe how many excitations have not yet decayed to the ground state, i.e. all remaining excitations, including those which cannot contribute to PL anymore. The PL signal represents only the amount of radiatively recombined carriers per unit time. However, the PL *kinetics* also reflect non-radiative losses [215,216,232]. This explains why all PL kinetics generally decay faster than the respective TA kinetics. In more detail, within the initial few ns the PL matches closely the TA signal. In this regime we expect mostly radiative exciton recombination to take place because (i) the ns-lifetimes characteristic for this process are observed and (ii) charge-neutral exciton traps, which would be the only other scenario where the PL kinetics would fully track the TA decay, are unlikely to play a major role in these high-PLQE materials. This predominantly radiative regime increases from about 5 ns for the undoped to about 15 ns for the highest doping concentration. For the longer time delays beyond approximately 200 ns all compositions follow a slow monoexponential decay with similar lifetimes. We assign this longlived component to non-radiative trap-assisted recombination [28,29]. The longer PL lifetimes upon doping indicate a reduction in non-radiative decay. The TA kinetics decay faster for the doped samples up to 50 ns, which is unexpected for reduced non-radiative recombination rates and a strong further indication for an increase in radiative rates. For time delays beyond 200 ns all samples show similar TA decays with longer lifetimes than the PL decays, suggesting a trap-dominated regime with long relaxation times and low radiative efficiency.

In order to quantify the underlying mechanism of enhanced radiative rates we next determine the oscillator strengths of the transitions from the absorption cross-sections. Therefore, we first calculate the average excitations per NC  $\langle N \rangle$  from two independent methods yielding similar values: one is a bulk-estimate based on the NC concentration and steady-state absorbance, while the other one is based on the assumption of a Poisson distribution of initial excitations in the NC ensemble. Both approaches yielded very similar results for  $\langle N \rangle$  as a function of excitation fluence in our experiments.

The first estimation is based on the sample's global properties, the NC concentration and steady-state absorbance. We know that the excitation fluence per pulse  $F_{ex}$  (in  $\mu$ J cm<sup>-2</sup>) is related to the laser power *P* used for photoexcitation of the samples in solution, the repetition rate  $R_{rep}$  and the beam spot radius  $r_{ex}$  through:

$$F_{ex} = \frac{P}{R_{rep}\pi r_{ex}^2}$$
(75)

The photon fluence per pulse *j* (in cm<sup>-2</sup>) is given by:

$$j = \frac{P\lambda\pi r_{ex}^2}{R_{rep}hc}$$
(76)

where  $\lambda$  is the excitation wavelength, *c* is the speed of light in a vacuum, and *h* is Planck's constant. The absorbed photon density per pulse  $j_{abs}$  (in cm<sup>-3</sup>) in the cuvette of pathlength *l* that is being absorbed can be inferred from measuring the UVvis absorbance *A* at the excitation wavelength and reads:

$$j_{abs} = j \frac{A}{l} \tag{77}$$

The density of NCs in solution  $\rho_{NC}$  (in cm<sup>-3</sup>) is related to the NC concentration  $c_{NC}$  (in mg mL<sup>-1</sup>) and the volume of a NC  $V_{NC}$  and the weight density of the material  $\rho_m$  via:

$$\rho_{NC} = \frac{c_{NC}}{V_{NC}\rho_{NC}} \tag{78}$$

Therefore, the average excitations per NC  $\langle N \rangle$  determined by this approach is:

$$\langle N \rangle = j_{abs} / \rho_{NC} \tag{79}$$

The second estimation is based on a Poisson distribution of initial excitations in the NC ensemble, where the average excitations per NC are directly related to the absorption cross-section  $\sigma \operatorname{via} \langle N \rangle = \sigma j$ .

Following the approach demonstrated by Klimov [215,233] and others [234,235], we assume Poisson statistics of photon absorption events to be valid, i.e. the initial occupancy of photo-induced excitations in a NC ensemble follows a Poisson distribution [236]. Thus, the probability p of a NC to contain i excitations at early times after excitation is:

$$p_i = \langle N \rangle^i / i! \ e^{-\langle N \rangle} \tag{80}$$

Hence, after multi-exciton recombination is completed, each NC cannot contribute to more than a single de-excitation event. We confirm that this is the case already at very early times after photoexcitation by performing ultrafast TA measurements, shown in Figure 61.

We extract biexciton lifetimes, which vary with composition between 10 and 25 ps, comparable with values reported in the literature [216].



Figure 61: Biexciton lifetimes extracted from fluence-dependent TA. (a) Example of procedure to extract biexciton lifetime: For a given composition, a low-fluence TA kinetics, where there is no significant biexciton contribution present, as well as a high-fluence kinetics is recorded. Then both are normalized to match their late-time single-exciton decay and subtracted from each other. (b)-(e) Monoexponential fits to the biexciton decay component for different doping levels, indicating an overall faster biexciton decay with increasing doping level, ranging from 25 to 10 ps lifetime.

As such, when analysing the long-time (ns-) TA kinetics, each NC cannot contribute to more than a single de-excitation event to be detected. Hence, when plotting the GSB intensity  $I_{TA}$ 

(after initial cooling and biexciton decay) as a function of photon fluence j (number of photons incident per cm<sup>2</sup>), we observe a saturation behaviour at high fluences (Figure 62).



Figure 62: Initial GSB within the ns-resolution of the experiment as a function of incident photon fluence. The absorption cross-section values  $\sigma$  extracted from fits (solid lines, see main text for details) increase with doping level. Samples were photoexcited with 3.1 eV pulses.

We can extract the average excitations per NC  $\langle N \rangle$  from the following saturation function by fitting the data based on the Poisson distribution model [233,236]:

$$I_{TA} \sim 1 - p_0 = 1 - e^{-\langle N \rangle}$$
 (81)

This allows us to determine the absorption cross-section as a function of composition as well. From our experimental TA data we find the absorption cross-section to increase with Mndoping level, yielding a nearly three-fold increase in the  $\sigma$  value for the highest doping concentration.

With the measured absorption cross-section, we can then directly access the oscillator strength f for the band-to-band transition (Figure 63), employing a modified version of the Strickler-Berg relation [237]:

$$f = \frac{8m_0 0.2303 n_m c^2 \varepsilon_0 \pi}{e^2 \lambda |F|^2} \sigma$$
(82)

where  $m_0$  is the free electron rest mass,  $n_m$  the refractive index of the medium, here toluene, c is the speed of light in a vacuum,  $\varepsilon_0$  is the vacuum permittivity, e is the elementary charge and  $\lambda$  is the wavelength of the optical transition.  $F = 3\varepsilon_m/(\varepsilon_s + 2\varepsilon_m)$  is the local field factor to account for the screening of the nanoparticle modelled as a sphere, with  $\varepsilon_m$  and  $\varepsilon_s$  being the dielectric constants of the medium and semiconductor, respectively.



Figure 63: Values of the oscillator strength per unit cell of the band-to-band transitions as determined from experimental absorption cross-sections (see text for details).

Since the oscillator strength quantity originates from a single-oscillator model, the values obtained were divided by the ratio of unit cell volume to NC volume before plotting, though the sum following the Thomas-Reiche-Kuhn rule could also be used [238,239]. We observe a threefold increase in the oscillator strength for the most doped sample. We find very similar values for the oscillator strength from the measured radiative rates, thus confirming our finding from two different sets of experiments, fundamentally connected via the Einstein relations [19]. The determined increase in oscillator strength, which is a direct measure of the dipole matrix element of the transition, can only be explained by two potential changes to the system upon doping: (i) changes in the dielectric constant of the material, which are highly unlikely given that only 60-80 atoms are substituted in our permille doping regime per nanocrystal ( $\sim 5 \times 10^5$  atoms); or (ii) the electron-hole overlap  $\Theta_{e-h}$  increases, which is given by [240]:

$$\Theta_{\rm e-h} = \left| \int \psi_e^*(r) \psi_h(r) dV \right|^2$$
(83)

where  $\psi_{e,h}(r)$  are the electron and hole envelop wavefunctions, respectively, which are integrated over the volume V.

Following an approach previously used for example by the groups of de Mello Donegá [212,214], or Kelley [241,242] and originally described by Efros and Rodina [240], the overlap integral is directly related to the oscillator strength and radiative rate via:

$$k_{r,X} = \frac{2e^4n}{\pi\varepsilon_0 m_0^3 c^3} |F|^2 \frac{m_0^2 E_g E_p \Theta}{3e^2 \hbar^2}$$
(84)

where e is the elementary charge, n the refractive index,  $\varepsilon_0$  is the vacuum permittivity, c is the speed of light in a vacuum,  $m_0$  is the free electron rest mass,  $\hbar$  is the reduced Planck's constant, and  $E_g$  is the energy of the optical transition.  $F = 3\varepsilon_m/(\varepsilon_s + 2\varepsilon_m)$  is the local field factor to account for the screening of the nanoparticle, assuming a random orientation of NCs with respect to the electric field of the interacting light. For simplicity, we modelled the NCs as spheres, with  $\varepsilon_m$  and  $\varepsilon_s$  being the dielectric constants of the medium and semiconductor, respectively. A more rigorous treatment of the electric field strength inside cubic nanocrystals can be found in ref. [43] Importantly, this will not influence the changes to the wavefunction overlap, since the same shape of NCs is maintained without and with doping, as checked with TEM.  $E_p$  is the Kane energy, usually found for III-V semiconductors to be on the order of 20 eV [215], but notably very close to 40 eV for CsPbX<sub>3</sub> perovskites due to the different orbital contributions to the valence and conduction band edges here, independent of halide choice [43].

The formal derivation of Eq. 84 can be found in the early works by Efros [240,243], and later also discussed together with Bawendi [244]. Importantly, we find that the measured increases in oscillator strength (from both TA and Tr-PL/PLQE) and thus also radiative rate *cannot* be explained by the only slight increase in bandgap and Kane energy upon Mn doping. This is because the doping level in the permille-regime is too small to significantly alter the global properties of the semiconductor, while still an exciton will experience the presence of a dopant, given that the distance between the distributed Mn ions is less than 5 nm and the exciton Bohr radius already approx. 2.5 nm (then followed by exciton diffusion as well). Thus, the overlap integral increases significantly in order to account for the enhancement observed experimentally.

We also directly rule out the frequently proposed influence of spin, that the paramagnetic  $Mn^{2+}$  species might have on the optoelectronic properties [216,230,245], by performing circularly polarised pump-probe spectroscopy, as illustrated in Figure 64.

In this modified version of (linear) transient absorption spectroscopy, the pump and probe beam paths include super-achromatic zero-order quarter-wave plates ( $\lambda/4$ ) to transform the linearly polarised beams into left- ( $\sigma^-$ ) or right-handed ( $\sigma^+$ ) circularly polarised light, depending on whether the wave plates are set to -45° or +45° with respect to the linear polarisation axis incident on them, respectively.



Figure 64: Sketch of a circularly polarised transient absorption setup. The quarter-wave plates ( $\lambda/4$ ) transform linearly polarised pump and probe beams to circularly polarised beams. The second quarter-wave plate after the sample transforms the circularly polarised probe beam after interaction with the sample back to linearly polarized light so that the detection geometry remains unchanged and reliable. Lin. Pol.: linear polariser,  $\lambda/4$ : quarter-wave plate.

This is achieved through the properties of a wave plate, which is a cut and polished slice of a uniaxial crystal, where the plane of the slice contains the extraordinary (or optic) axis. An input beam that is normally incident on the wave plate will be resolved into ordinary and extraordinary axis components, each with a different refractive index ( $n_o$  and  $n_e$ , respectively). Therefore, the beam that emerges has a phase-delay difference (retardation) between the axes, given by:

$$\Gamma = \frac{2p}{\lambda} (n_e - n_o) L$$
(85)

where the wave plate thickness L is chosen such that the retardation ( $\Gamma$ , in radians) corresponds to  $\pi/2$  (90°), or a quarter of a 360° full wave. This phase-shift will result in the conversion of linearly polarised light to circular and vice versa [246]. A second quarter-wave plate after the sample is employed to transform the probe beam back to linear polarisation and as such won't alter the detection beam path. This is especially important, since the spectrometer grating's efficiency as well as Fresnel-losses at the detection beam path optics will be highly polarisation-dependent.

As illustrated in Figure 65, employing circularly polarised excitation offers insights into the spin-dependent optically allowed electronic transitions of semiconductors.



Figure 65: Optically allowed transitions probed by circularly polarised light. The state notation is written as  $|J, m_j\rangle$  where J = 1/2 is the electron's total angular momentum quantum number and  $m_j = \pm 1/2$  is its projection in the z axis. Absorption of a pump photon will raise the angular momentum by  $+\hbar$  ( $\Delta m_j = +1$ ). Conversely, emission of a photon from the excited states in the form of photoluminescence (PL) reduces the angular momentum by  $\Delta m_j = -1$ .

Since the right-handed ( $\sigma^+$ ) polarised photon carries an angular momentum of  $+\hbar$  (in the direction of propagation), the absorption of such a photon will raise the angular momentum of the electron, increasing the projection of its total angular momentum quantum number (J) in the z axis to  $\Delta m_j = +1$  in accordance with total angular momentum conservation [246]. While the circularly polarised pump defines the spin orientation of the charge carriers in the sample, each probe polarisation in transient absorption will trace the different  $m_i$  states.

By imposing these restrictions to optical selection rules onto the system, Figure 66 shows the resulting polarised carrier dynamics of the nanocrystals with varying composition. Since all

kinetics follow a very similar shape, the individual data traces before processing are only displayed exemplary for the 1.9‰ doping-level composition.



Figure 66: Depolarisation dynamics of ground-state bleach signal from circularly polarised TA. The pump and the probe beams were circularly polarised through sets of linear polarisers and quarter-waveplates, respectively. (a) Representative co- and counter polarised configurations for the 1.9‰ doping-level composition, indicating a prompt decay for the co- and a delayed decay for the counter-configuration, respectively. The kinetics are normalised to their late-time decays. (b) Subtraction of the normalised kinetics in (a) yields depolarisation lifetimes ranging from 1.4 to 1.9 ps with no significant influence of the Mn-doping level. The average depolarisation lifetime is 1.6 ps. Measurements were performed at room temperature.

We observe no significant difference in depolarisation lifetimes between all compositions, with an average lifetime of ~1.6 ps. We note that this lifetime is shorter than previously published results using this technique on bulk MaPbI<sub>3</sub> material of about 7 ps [247]. This can be explained by the smaller exciton binding energy in their material compared to our nanocrystals, as well as the temperature-difference, since they conducted measurements at ca. 77 K, while we measured at room temperature, hence potentially reducing depolarisation lifetimes through enhanced phonon scattering. Thus, no strong dopant-host exchange coupling appears to be present in our samples. If there is a certain degree of coupling that we cannot detect, it is too weak to significantly influence the optoelectronic properties that determine device performance. Instead, the local distortion of the perovskite lattice induced by the Mn dopants breaks the lattice periodicity in the interior of the NC and creates localisation sites for the photo-generated excitons, which leads to higher values for the electron hole overlap and thus probability of radiative decay. Assuming no changes to the dielectric constant, we find  $\Theta_{e-h}$  to increase by 158% for the highest doping level (see also refs. [240,243]). To further probe the proposed influence of Mn-doping on exciton recombination, we perform electronic structure calculations using density functional theory (DFT, for details see Methods Chapter above). Via the supercell approach, we model bulk pristine and Mn-doped CsPbX<sub>3</sub> compositions for X = Cl, Br or a mixture thereof. We first confirm a direct bandgap at the Rpoint of the Brillouin zone, which upon doping increases by  $\sim 0.2$  eV in agreement with the experimentally determined values. In line with previous reports [80,248], the valence band maximum (VBM) of the undoped composition is mainly composed of antibonding hybrids from Pb 6s and halide p orbitals, while the conduction band minimum (CBM) consists mainly of empty Pb 6p orbitals. However, once the Pb is partially replaced with Mn in the doped compositions, the VBM is perturbed, resulting in a band that mostly resembles the energetically lower lying isolated halide p orbitals. At the same time, the perturbation in the periodicity of the Pb 6p orbitals leads to the destabilisation of the CBM compared to the undoped case. Both perturbations hence contribute towards the observed widening of the bandgap. Notably, the bandgap of the doped compared to the undoped material was expected to increase also because of the additional chloride added to the lattice, thus changing the halide ratio of the material slightly and thus tuning the bandgap as common in halide perovskites. However, since we only alter up to a few permille of atoms, the additional chloride incorporated through our doping levels would be too low to account in full for the observed blue-shift. Moreover, from STEM and XRD data we find no indication of a change in nanocrystal size or shape upon doping, which could imply increasing confinement to be driving the blue-shift. Thus, the significant widening of the bandgap we observe can be mostly assigned to the lattice periodicity breaking from the manganese dopants.

Importantly, these Mn-induced perturbations also reduce the dispersion of both VBM and CBM, indicating a more localised electron and hole state with higher effective masses in the doped case. To identify the element-specific changes that occur through the substitution of Pb for Mn, we calculate the real-space charge distribution of the CBM for pristine and Mn-doped CsPbCl<sub>3</sub> using the PBEsol functional with 20% additional Hartree-Fock exchange (Figure 67). We observe that the charge distribution shows a more localised character compared to the undoped case with the largest coefficients in proximity to the central Mn atom and along the Mn-Cl-Pb bonds, while the contributions from the remaining perovskite scaffold become negligible. This charge localisation corresponds to an increased electron hole wavefunction overlap and thus increases the probability of radiative recombination [18] upon doping, observed experimentally.



Figure 67: First-principles calculation of the real-space charge density for pristine (left) and Mn-doped perovskite (right), showing carrier localisation at the manganese dopant. Shown is the charge distribution of the conduction band minimum that is located at the high-symmetry point R (0.5, 0.5, 0.5). Left: the conduction band minimum is generated by hybridisation of unoccupied Pb 6p orbitals that are fully delocalised across all Pb centres. Right: the conduction band minimum now significantly mixes with the Mn 4s orbital which is energetically aligned with the Pb 6p states. Additional hybridisation with the 3p orbitals of the complexing Cl atoms leads to an isotropically localised state around the guest atom. Value at isosurface is  $2.36 \times 10^{-3} e \text{ Å}^{-3}$ . Calculations performed by Ivona Bravić.

The origin of this localisation effect is found in the projected density of states (pDOS), shown in Figure 68. Here, the Mn 4*s* states as well as the Mn 3*d* states energetically coincide with the CBM of the perovskite but intriguingly, while the 3*d* orbitals have a negligible effect on the band edge, the 4*s* orbitals strongly hybridise with it and thus modify the host wavefunction significantly. This significant hybridisation of the Mn 4*s* states with the host leads to charge localisation, responsible for the observed radiative rate increases, while the Mn 3*d* states do not mix with the CBM and hence form a competing decay channel at higher concentrations.


Figure 68: Projected density of states for CsPbCl<sub>3</sub> (left) and CsPb<sub>0.963</sub>Mn<sub>0.037</sub>Cl<sub>3</sub> (right), both calculated from first principles with the PBEsol functional including 20% Hartree-Fock exchange. We find significant hybridisation of the Mn 4*s* states with the host which leads to charge localisation, responsible for the observed oscillator strength increases. Calculations performed by Ivona Bravić.

We further find that the hybridisation of the Mn 4*s* orbitals with the host shown here for the Mn-doped pure-chloride composition is halide-dependent (Figure 69).



Figure 69: Projected density of states for (a) CsPb<sub>0.963</sub>Mn<sub>0.037</sub>Cl<sub>3</sub>, (b) the (Cl,Br) mixed-halide version thereof, and (c) its pure-Br analogue, calculated with PBEsol+U ( $U_{eff} = 3.5$ ) by Ivona Bravić.

With increasing Br concentration, the unoccupied perovskite states shift towards lower energies, while the Mn 4*s* states remain invariant. This off-set of the relative energies causes a reduced hybridisation. The resulting loss in localisation could explain why similarly beneficial doping effects on the radiative rate of the perovskite NCs have not been reported in the literature for pure-bromide compositions so far.

Further, we observe that the relative position of the vacant Mn 3*d* states is not only dependent on the Mn concentration but on the halide content, too: With increasing Br content, the unoccupied Mn 3*d* orbitals are pushed towards higher energies, such that *d-d* transitions that were previously lying within the host bandgap become inaccessible as an alternative decay pathway. This suggests that a balanced halide ratio and distribution is beneficial in order to suppress this host exciton decay channel. We conclude that both the Mn *and* the halide concentration are levers that can be used to tune localisation and thus PLQE. This further points towards MnCl<sub>2</sub> acting not only as a means to fill halide vacancies and reduce trap densities that cause non-radiative decay, but more importantly to engineer the exciton wave function for optimised radiative yields through the halide ratio and distribution of Mn centers.

To summarise this section, we find two aspects to the effect of doping on the localisation of the wavefunction that constitute the band edges of the perovskite: a structural and an electronic one.

The first effect is the lattice-periodicity breaking, which is generally caused by any B-site substitution and is therefore not metal-specific. The periodicity breaking pushes both the valence band maximum and the conduction band minimum towards the atomic limits. This leads to less dispersive band edges compared to the undoped case and hence more localisation. The second effect, which, for Mn specifically, turns out to be stronger, is the mixing (hybridisation) of the dopant with the perovskite states that form the band edges of the system. It turns out that an important prerequisite for hybridisation is the relative position of the empty Mn *s* states and the conduction band minimum. Here we observe that the band alignment does depend on both the metal dopant's electronic structure, and also on that of the chosen halide. With increasing chloride (and decreasing bromide) content the Mn *s* state and the conduction band edge come closer to one another in energy, such that hybridisation, and thus localisation, becomes possible. Therefore, it is not only important to consider the choice of the metal dopant, but also of the halide to exploit the electronic-induced localisation effect and hence maximise the radiative rate.

Lastly, we note that the use of other transition metals as dopants could be a promising avenue to tackle the challenges mentioned above: By tuning the element-dependent degree of *s*-orbital

hybridisation and mitigating the formation of *d*-states *via* the choice of closed-shell ions, the localisation effect we observe can be exploited to maximise radiative rates.

## 5.3 Conclusions

We report that manganese-doping of perovskite nanocrystals increases their luminescence yields due to two effects: First, the reduction of non-radiative rates discussed in the literature before, likely through trap-passivation at low Mn doping densities up to  $\sim$ 1.9‰, where we do not yet observe Mn cluster formation and their broad *d-d* emission. Secondly, we find an unexpected increased radiative recombination rate of excitons induced by the Mn dopants. We can attribute the enhanced luminescence rates to increased oscillator strength from stronger charge carrier localisation, with a concomitant increase in overlap of electron and hole wavefunctions, thus enhancing the radiative recombination of excitons in the vicinity of the dopants. We stress that this localisation effect provides a pathway to improve radiative rates even for materials, which may have already reached very small trap densities through advanced fabrication methods. Our results demonstrate that transition-metal doping provides detailed control of electronic structure and exciton dynamics in metal-halide perovskite nanocrystals and opens a route towards very efficient light-emitting devices.

## **Chapter 6: Conclusions and Outlook**

In this thesis I have expanded the current state of knowledge of the behaviour of charge carriers in a novel class of semiconductors based on metal-halide perovskites. This family of materials has shown a remarkable surge of interest in the last ten years due to their unexpectedly high performance in optoelectronic applications like solar cells and LEDs.

In contrast to most semiconductors employed commercially to date, namely silicon and III-V compounds, metal-halide perovskites can be readily processed from solution at low temperatures, and owing to its unique electronic structure and lattice softness will still only have a moderate density of – mostly shallow – traps, thus maintaining high power conversion efficiencies. Moreover, due to the intrinsically high absorption of these materials, perovskites can be employed in thin-film technologies, allowing for flexible and light-weight future applications.

After a brief review of the fundamental concepts in semiconductor and device physics, we discussed the structural and electronic properties of metal-halide perovskites needed to put the results of the experiments carried out in this PhD into context. Then we discussed the methods used to carry out the studies on charge carrier dynamics in semiconductors, with a focus on time-resolved optical spectroscopy.

We studied two distinct perovskite-based material systems and found evidence for charge localisation in both cases, yet with fundamentally different origin, mechanism and consequences.

In the first study, we investigated a variety of the most commonly encountered perovskitebased thin films. They supposedly adopt a bulk perovskite structure, with different cations – methylammonium, formamidinium, and cesium – and a mixture of iodide and bromide anions. We also studied samples containing rubidium- and potassium-additives. While these cations are too large to be incorporated successfully into the crystal lattice, they do have shown to lead to increased optoelectronic performance assigned to a trap-passivation mechanism.

We have used transient absorption and photoluminescence experiments to show that the carrier-density dependence of the photoluminescence – a bimolecular recombination process of electrons and holes – is unexpectedly described by quasi-first order kinetics, but only for compositions including mixed halides. We used temperature-dependent luminescence measurements to exclude an excitonic origin of this first-order behaviour, in line with previous

reports of effectively free charge carriers in these systems with very low exciton binding energies. Instead, we found a temperature-activated PL dependence, much resembling a de-trapping process.

We employed PL confocal microscopy to reveal an energetically disordered spatial landscape with domains that are several microns in size, featuring a partly higher and partly lower optical bandgap than the average one measured globally. Using electron-probe microanalysis we correlated these domains to a locally higher or lower ratio of iodide to bromide, which varies the bandgap.

This explains the PL trends observed from time-resolved experiments: the photoexcited charges funnel into the local potential minima and accumulate there. If then an opposite charge diffuses into these sites of locally high carrier density, the kinetics will be dominated only by the minority carrier density, much like in a doped system, and behave quasi-linearly.

Next, we fabricated transistors using the different perovskite compositions and could extract from the current-voltage characteristics that mostly holes become localised, while electrons remain mobile. Supported by DFT calculations, we confirmed that the modulation of the bandgap is mostly a consequence of the valence band structure changing, favouring hole accumulation, while the conduction band mainly consists of lead p orbitals and thus remains largely unaffected by the changing halide environment.

This charge localisation can be indeed a beneficial effect, since the carrier density will locally remain high, even at low excitation conditions or injected currents, thus outcompeting trapdominated recombination and maintaining the desirable radiative recombination regime. This can be directly observed from excitation-density-dependent photoluminescence quantum yield measurements whose values level out at a high level even at lowest carrier densities. We have thus shown that the 'messy' fabrication of these multi-component alloys and the connected disordered energy landscape can in fact be beneficial for device performance.

Future research based on this study should include a detailed computational analysis of the charge carrier dynamics depending on the domain size, distribution, and energetic off-sets, so as to maximise the global PLQE. With this knowledge, a directed micro-patterning approach based on established lithography techniques or evaporation methods using structured masks will help to push device performance levels in solar cells and LEDs alike to their fundamental limits.

In the second study, we moved to a semiconducting system where charges are spatially confined. Based on the bulk perovskite structure of cesium lead chloride-bromide, in this case colloidal solutions of nanocrystals were investigated. We here focussed on perovskite nanocrystals where a small amount of lead ions – on the permille-level – has been substituted for manganese ions. Similar to earlier reports, upon manganese-doping the observed photoluminescence intensity increased dramatically by more than two-fold, compared to the undoped case. Moreover, beyond a certain threshold concentration of manganese ions, no further gains in the original host luminescence band were observed, but instead a second, long-lived low-energy emission band appeared.

The origin of this slow and broad additional radiative channel was shown to lie in the spin- and Laporte-forbidden *d-d* transition of the octahedral manganese complexes formed. They become observable at higher doping levels where this additional relaxation pathway competes with the primary one formed by the host's band-to-band transition.

From structural characterisation we confirmed the successful incorporation of manganese ions into the perovskite lattice for low doping concentrations, and estimate charges to be in the weak quantum-confinement regime according to the size of the crystallites. We also confirmed the existence of excitons as the primary photo-excited species from fluence-dependent photoluminescence measurements.

Intriguingly, by comparing PLQE and time-resolved PL data, we found that, not only does the non-radiative recombination rate of the excitons decrease upon doping, but the radiative rate was shown to increase as well. This is in contrast to previous reports that assigned the performance gains in doped perovskite nanocrystals to a trap-passivating mechanism, which reduces loss channels. Instead, the radiative excitonic recombination rate is considered to be an intrinsic material property that is generally hard to control.

Assuming a Poisson distribution of photo-excited states in the nanocrystal ensemble, we could extract the doping-dependent absorption cross-section from transient absorption measurements and determine the oscillator strength of the optical band-to-band transition. We found that the oscillator strength increases in line with the gains in radiative recombination and, supported by first-principles calculations, could relate this to a localisation of charges around the dopants. The manganese-ions break the lattice periodicity locally and thus increase the electron-hole overlap around these sites, such that the radiative recombination rate increases in accordance with Fermi's golden rule. This originates in the hybridisation of manganese *s* orbitals with the lead-halide host bands, whereas the manganese *d* orbitals do not hybridise with them and form a separate energy band, acting as an alternative recombination pathway instead.

This effect of carrier localisation by means of 'wavefunction engineering' through a straightforward synthetic doping step could well be generalised as a new strategy towards highly efficient LEDs, not limited to the use of manganese ions.

Future work should thus explore other transition-metal dopants. Choosing, for example, dopants with a closed-shell system could exclude the formation of the undesired relaxation pathway observed for manganese doping. Conversely, iodide-based perovskite nanocrystals would have a lower bandgap than the manganese orange emission band and could therefore be expected to avoid this loss channel as well, while still benefitting from the excitonic localisation effect induced by the dopant, provided a sufficient orbital overlap can be maintained. By choosing elements whose electronic structure is tailored to match that of the host semiconductor, this material platform not only provides a playground for studying exciton physics and energy transfer mechanisms, but also offers a route towards more efficient low-cost photonic sources.

To conclude, we have investigated two next-generation material platforms based on metalhalide perovskites, studied the fate of charges in these semiconductors, and discovered that localisation effects can play an important role in their optoelectronic performance. The research presented in this thesis will hopefully stimulate progress in the mechanistic understanding of semiconductor photophysics and also in the development of more efficient devices for a sustainable energy future.

## **List of Publications**

- Photodoping through local charge carrier accumulation in alloyed hybrid perovskites for highly efficient luminescence.
   Feldmann, S., Macpherson, S., Senanayak, S. P., Abdi-Jalebi, M., Rivett, J. P. H., Nan, G., Tainter, G. D., Doherty, T. A. S., Frohna, K., Ringe, E., Friend, R. H., Sirringhaus, H., Saliba, M., Beljonne, D., Stranks, S. D., Deschler, F.
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- Tailored local bandgap modulation as a strategy to maximise luminescence yields in mixed-halide perovskites.
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- Manganese doping for enhanced magnetic brightening and circular polarization control of dark excitons in paramagnetic layered hybrid metal-halide perovskites.
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