Monocrystalline halide perovskite nanostructures for optoelectronic applications

Khoram, P.

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Introduction

The social and technological development of today’s modern society is not imaginable without optoelectronic devices— the electronic devices that convert, emit, detect or control light. Our every day lives are surrounded by light emitting diodes (LEDs), laser-based telecommunication systems, high mobility transistors, and photovoltaics. The ambitious goal of controlling the ever growing energy consumption while proceeding with high-technology life is only possible with developing new designs and materials for low-cost and efficient optoelectronics. The incorporation of nanotechnology and nanomaterials into these devices opens up additional and unique opportunities for approaching highly efficient devices. Less than a decade ago, halide perovskites were only a class of ionic crystals among many others, with interesting properties, but not much speculation about their applications. Their initial success in delivering high efficiencies in solar cells brought them to the forefront of optoelectronics research recently. Besides the promise for a new generation of efficient photovoltaics and light emitting devices, their complex system has intrigued the curiosity of many scientists. Studying perovskites in their fundamental details can also potentially initiate the discovery of devices with new designs and applications. In this thesis we attempt to contribute to unravelling the unknown aspects of halide perovskites towards their optoelectronic application by fabricating and characterizing mono-crystalline perovskite nanostructures. We start this chapter by giving a historical background and introducing the chemical structure of perovskites. Afterwards we discuss the special optical properties that their ionic nature bring to them. We explain then the charge carrier generation and
recombination in halide perovskites and continue with reviewing the advances of perovskites in optoelectronics. Next we go through perovskite nanostructures and single crystals and their incorporation into devices. Subsequently we finish this chapter by providing an outline of the following chapters in this thesis.

1.1 Brief history and crystal structure of perovskites

In 1839, Gustav Rose discovered CaTiO$_3$ mineral in Ural mountains of Russia and named it Perovskite after the mineralogist Lev Perovski [1]. This discovery opened up a new category of materials all with the same crystal structure as CaTiO$_3$, known as the perovskite structure [2]. These materials with the stoichiometric formula of ABX$_3$ all consist of three ions: A and B cations and X anions. The perovskite structure can be represented in many different ways. Figure 1.1a shows a usual ball-and-stick model showing the unit cell of the perovskite, where A atom is in the center of a cubic unit with B atoms in the 8 corners and X atoms in the middle of each edge. Another common way to show the unit cell of the perovskite structure is with X anions octahedrally coordinated around the B cation, with A cations in the corners of the unit cell as shown in Figure 1.1b. Sometimes the 3-dimensional structure is pictured with corner-sharing BX$_6$ octahedra network with A ions sitting in cuboctahedral cavities. The nature of A cations including its polarity, charge and size,[3] and also their interaction with the inorganic framework [4] defines the tilting and rotating of the BX$_6$ in the lattice and creates cubic, tetragonal or orthorhombic phases(Figure 1.1c-d). A certain perovskite goes through phase transition by external parameters such as temperature, pressure and magnetic and electric fields which control these tilts and rotations. A wide range of ions (elements and compounds) can mix and form perovskite structures, as long as the charge balancing is maintained and the sizes of ions can preserve the perovskite structure. Goldschmidt tolerance factor [5] and the octahedral factor [6] are commonly used to predict the probable formation and crystal structure of perovskites based on the ionic radii and the ideal distances between ions. Goldschmidt factor (t) is given by the equation below:

\[
t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}
\]

(1.1)

where \( r_i \) is the ionic radius of A, B or X. The octahedral factor \( \mu \) is given by the ionic radii of B and X in BX$_6$ octahedra as follow [7]:

\[
\mu = \frac{r_B}{r_X}
\]

(1.2)

The \( t \) and \( \mu \) values should lie between 0.75 – 1.0 and 0.42 – 0.8 respectively for the
1.1 Brief history and crystal structure of perovskites

A+ cation
B2+ cation
X- anion

Figure 1.1: Schematic of various representation of perovskite crystal structure.

a) The unit cell of perovskite structure, where A atom is in the center of the unit cell with B atoms in 8 corners and X atoms in the middle of edges
b) The perovskite unit cell with BX₆ octahedron in the center and A atoms in the corners of the unit cell.
c), d) and e) show corner-sharing BX₆ octahedra networks of perovskite structures with orthorhombic, tetragonal and cubic structure, respectively. With increasing the temperature the phase transition occurs from orthorhombic to tetragonal and cubic. The middle row is the ac-plane and the bottom row is the ab-plane.

formation of oxide perovskite structures [7].

Nowadays, the term perovskite is not only attributed to CaTiO₃, but is a general name for any ABX₃ material with perovskite structure. Many other minerals such as SrTiO₃ and LaCoO₃ are in the same category [8]. Halide perovskites are similar to oxide perovskite but the oxygen is substituted with a halogen, such as chlorine, bromine or iodine and the valence of the cations is adjusted to maintain charge neutrality. This class of perovskites was first studied at the end of the nineteenth century by Wells [9]. When a halogen replaces oxygen in the X site, the oxidation state of A and B cations must sum to 3, therefore monovalent A and divalent B ions are required. Both tolerance factor and octahedral factor can also be used to predict the formation of ABX₃ halide perovskites with 96% predicting accuracy [10]. The octahedral factor has a lower limit, and both factors have to be satisfied but they
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are not sufficient for the formation of perovskite structure [7, 10].

Almost a hundred years after the early demonstration of inorganic halide perovskites, Weber replaced the A ion with an organic cation and introduced methylammonium lead halides with the chemical formula CH$_3$NH$_3$PbX$_3$ (X=Cl, I or Br) as the first hybrid halide perovskites [11, 12]. To predict the perovskite formation with the geometrical factors, the effective radius of the organic cation is considered as a rigid sphere model. For the formation of halide perovskites 0.81 < $t$ < 1.1 and 0.44 < $\mu$ < 0.90 should be satisfied. Studies showed that the cubic structure of hybrid halide perovskite is realized when 0.85 < $t$ < 1.0 [13]. CH$_3$NH$_3$PbI$_3$ as the most common hybrid perovskites used in optoelectronics has a lower $t$ of 0.83 and therefore the less symmetric tetragonal crystal structure at room temperature. When iodide is replaced with the smaller bromide or chloride ions, the $t$ factor falls in the right range for a cubic structure. In general, all CH$_3$NH$_3$PbX$_3$ perovskites have a cubic structure at higher temperature, and transform to tetragonal and orthorhombic structures subsequently by lowering the temperature.

Due to the larger ionic radii of halide ions in comparison to the oxides, only a limited range of divalent cations can maintain the perovskite structure in this system including the alkaline earths, rare earth and group 14 elements such as Pb$^{2+}$ and Sn$^{2+}$ ions. The charge distribution of the A cation also plays an important role in stabilizing the hybrid halide perovskite structure. In addition to methylammonium, formamidinium (H$_2$NCHNH$_2$$^+$) and mixtures of organic and inorganic cations (CH$_3$NH$_3$$^+$, H$_2$NCHNH$_2$$^+$ and Cs$^+$) are among those which form stable and efficient hybrid perovskite systems for optoelectronics [14].

The fabrication and semiconducting properties of layered and 3-D halide perovskites were first studied in the 1990s by Mitzi et al [15–18]. However, not much attention was paid to the application of materials in optoelectronic devices until recently. In 2009, Miyasaka’s group [19] applied hybrid halide nanocrystals as visible-light sensitizers in a liquid electrolyte based dye sensitized solar cell (DSSC). In this early demonstration the efficiency was as low as 4%, although this was just the starting point of the rapid development of halide perovskites-based devices. Within only 8 years, the PCE of perovskite solar cells has increased to values comparable to those of silicon solar cells, the most common photovoltaic technology [20]. Although halide perovskites were considered primarily to replace the dye molecules and organic absorbers in DSSCs, nowadays perovskite solar cells stand out as an independent type of solar cell with a planar thin film architecture.

The rapidly increasing PCE of perovskite solar cells drew the attention of numerous research groups worldwide to halide perovskites as the active component of other optoelectronic devices as well during the last 8 years. In addition to tremendous efforts in increasing the device performance [21–27], many research groups used
1.2 The ionic nature of halide perovskites

Perovskites are ionic solids and their chemical bonds are formed based on electrostatic forces between the oppositely charged ions. This characteristic makes halide perovskites fundamentally different than conventional inorganic semiconductors with covalent bonds. In covalent solids, such as those formed from elements of group 14 like Si and Ge, the shared electrons construct the bonds which keep the counterparts of the solid together. The interactions of electrons with each other and the neighboring atoms in the solid, defines many physical properties of the solid such as hardness, melting and boiling points, solubility, and conductivity [33]. We should note that often the bonds in solids have a complex nature of mixed binding types, for instance TiO$_2$ has ionic/metallic bonds. But it is common to ignore this in discussion of the solid structures for simplicity and only consider the dominant bond type [34]. Here we also take this assumption for the further discussion of bonds and their effect on electronic structure in halide perovskites.

Electrons in solids have discrete ranges of energies, similar to electrons in isolated atoms with specific available orbitals. When atoms are brought together to form solids, the electrons feel the nuclei and electrons of neighboring atoms as well, which cause the overall wave functions of electrons to be altered. In formation of ionic solids electrons are exchanged between positive and negative ions in order to make the outer orbital of ions full with the electronic structure of inert gases. For example in the simplest and well-known case of NaCl, Na with electron configuration of $[Ne]3s^1$ gives away its valance electron to the Cl with electron configuration of $[Ne]3s^23p^5$. This way Na$^+$ and Cl$^-$ ions with electron configuration of inert gases (Ne and Ar) are formed and the coulombic attraction of ions hold them together in the lattice [33]. In most ionic structures, electrons are tightly bound to each atom and are not free to contribute to the current flow. In fact, ionic solids are mostly insulators. In the band structure of ionic solids which comes from the participation of valance electrons, the energy difference between the valance band and conduction band is usually as high as 3 eV or more. Surprisingly that is not the case in the electronic structure of halide perovskite solids. In the halide perovskites, as the most relevant perovskites for optoelectronics, the valance band maxima (VBM) form as the result of $\sigma$-antibonding of the metal outer $s$ orbitals (Pb 6$s$ or Sn 5$s$) with halide outer $p$ orbitals. Conduction band minima (CBM) mostly comes from the $\sigma$-antibonding of metallic ion $p$ orbitals (Pb 6$p$ or Sn 5$p$) with a small contribution.
of halide outer $p$ orbitals ($5p$ for I, $4p$ for Br and $3p$ for Cl). The formation of CBM bands dominantly from metallic $p$ orbitals gives halide perovskites a unique dual ionic and covalent nature. The energy gap of such electronic configuration is less than 3 eV, classifying halide perovskites as semiconducting materials.[35, 36]

The electronic band structure of halide perovskites gives them distinct characteristics from conventional semiconductors and brings them special properties. Density functional theory (DFT) calculations of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and mixed halide perovskites [37], along with earlier first-principle pseudopotential calculations of the electronic band structure of $\text{CH}_3\text{NH}_3\text{PbX}_3$ and $\text{CsPbX}_3$ [36] indicate that the band structure near the VBM and CBM is mainly formed from the $[\text{PbX}_6]^{4-}$ inorganic framework, with organic cations playing a minor role. These findings were consistent with later experimental evidence of the band structure from UV-Vis spectroscopy in halide perovskites [38]. Filip et al [39] showed by DFT calculations that the bonding and antibonding bands of the A cation are located away from the band edges, as shown in Figure 1.2a. They indicated that removing the cation while compensating the charges by a positive background, and keeping the arrangement of octahedral network (bond length and tilt) the same, does not change the band structure around the band edge significantly.

Formation of the band gap from the contribution of the different ions in perovskite semiconductors gives an interesting feature to these materials: the possibility to tune the optical properties via changing the ionic components. The energy and structure of perovskites’ band gap can be tuned by substitution of different ions in each A,B and X sites and even making a combination of different ions with varied ratios in each site. Since the early development of hybrid perovskite photovoltaics, many researchers mixed halide ions (Cl, Br, and I) to obtain a range of band gap energies from 3.11 eV in ultra-violet (from $\text{CH}_3\text{NH}_3\text{PbCl}_3$ ) to 2.23 eV in visible ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) and 1.55 eV in infrared ($\text{CH}_3\text{NH}_3\text{PbI}_3$) [41–48] (see Figure 1.2a). The increase of band gap with reducing the halide ionic size has been used as a general trend also in other halide perovskites, such as $\text{CsPbX}_3$ [49–51], $\text{CH}_3\text{NH}_3\text{SnX}_3$ [52, 53] and $\text{H}_2\text{NCHNH}_2\text{PbX}_3$ [54].

Substitution of the metallic ions has an anomalous effect on the band gap. When Pb and Sn are mixed on the B sites, the band gap of the compound does not lie between the energies of the pure $\text{APbX}_3$ and $\text{ASnX}_3$ [55]. This effect enables broadening the range of band gaps that halide perovskite can achieve.

Considering the band gap structure of perovskites arises mainly from the $[\text{BX}_6]^{4-}$ octahedra network, it may seem that A$^+$ cations have only a stabilizing role and their effect on electronic structure is negligible. If that was the case, replacing smaller Cs$^+$ with $\text{CH}_3\text{NH}_3^+$ would make the band gap just slightly higher, because of the increase in the lattice constant [56]. However, the optical experiments show the band gap decreases from 1.73 eV to 1.55 eV and 1.48 eV for $\text{CsPbI}_3$ to $\text{CH}_3\text{NH}_3\text{PbI}_3$.
1.2 The ionic nature of halide perovskites

Figure 1.2: Electronic band structure of halide perovskite and effect of ionic components on its band gap. 

a) Electronic band structure of CH$_3$NH$_3$PbI$_3$ in low-temperature orthorhombic phase with (black lines) and without (blue lines) organic cation calculated by DFT. The left part of the graph shows the partial density of states, and indicates the contribution of orbitals of each ion in the formation of the band structure. The VBM consists of I$^5p$ states and the Pb$^6s$ states. The CBM consists mainly Pb$^6p$ and I$^5p$ states. Reproduced from Ref. [39] with permission from Springer Nature.

b) Band gap tunability of CH$_3$NH$_3$PbX$_n$Y$_3$–$n$. The emission of the CH$_3$NH$_3$PbX$_n$Y$_3$–$n$ perovskite is tunable from 390 to 790 nm wavelength. Reproduced from Ref. [40] with permission from Springer Nature.

and then H$_2$NCHNH$_2$ PbI$_3$ respectively. Filip et al. [39] showed that the type and steric size of A$^+$ cation influences not only the lattice size, but also X-B-X bond angle [39]. On the other hand, the chemical interaction of the A$^+$ cation with the [BX$_6$]$^{−4}$ octahedra affects the ionic-covalent nature of chemical bonds. For example, increasing the hydrogen bonds of organic cation make the X-B (metal-halide) nature more ionic, and the VB and CB structures are getting more influenced by metal (Pb or Sn) [57]. Here the spin-orbit coupling from the heavy metals become more significant and decreases the band gap when going from smaller CH$_3$NH$^+_3$ to the larger H$_2$NCHNH$_2^+$. Overall, halide perovskites benefit from defect tolerance which originates from their special band structure. The antibonding coupling of Pb lone-pair s orbitals
and halide $p$ orbitals cause structural defects such as iodine and methylammonium vacancies forming energy levels outside of the forbidden band gap [58]. This characteristic gives them less defect density in the forbidden band gap compared to more covalent crystalline semiconductors such as CdTe and Cu$_2$ZnSnS$_4$ [59, 60]. However, the formation of defects within the conduction and valance band has its own consequences, for example it brings above band gap absorption [59].

### 1.3 Charge carrier dynamics in halide perovskites

Upon excitation of a semiconductor, the charge carriers are generated via the transfer of electrons from valance band to the higher-energy conduction band (Figure 1.3a). Eventually, the electrons and the holes recombine and release the energy difference between the excited state and the ground state in various energy forms, depending on the recombination process. These processes are schematically illustrated in Figure 1.3b.

In the trap-assisted recombination, a charge carrier (electron or hole) is captured

![Figure 1.3: Charge carrier generation and recombination mechanisms in semiconductors. a)electron and hole are generated in the semiconductor upon optical excitation with photons with higher energy than semiconductor's band gap. b) The electron and hole recombine via various possible recombination mechanisms: (i) Trap-assisted recombination is a monomolecular process when the charge carrier is trapped in an extra energy level within the forbidden band gap, formed due to defects or impurities. (ii) Bimolecular recombination is the band-to-band transfer of electrons from conduction band (CB) to the valance band (VB) which is followed by the release of energy as a photon. (iii) Auger recombination occurs at the high charge carrier density. The electron and holes recombine band-to-band but the energy of the process is given to a third particle.](image-url)
in a trap state within the forbidden band gap of the semiconductor. In this process, the energy of the excited state is given off in the form of heat to the lattice phonons. These trap states are usually formed due to the impurities or structural defects in the lattice of the semiconductors. The recombination through the trap states is also referred to as Shockley-Read-Hall (SRH) process\[61, 62\]. The interruption of the lattice and presence of dangling bonds at the surface can potentially introduce a large density of trap states and make the surface a source of non-radiative recombination in semiconductors\[63\]. In general, reducing trap states lowers the non-radiative recombination rate, increases the effective lifetime and diffusion length of charge carriers, and boosts the performance of devices. Therefore it is important to recognize the contribution of trap states in the surface and bulk of a semiconductor separately and choose the proper strategies to reduce them in each.

Bimolecular recombination occurs when an electron directly fills the hole in the valence band. The energy of this process is released as a photon with an energy equal to the band gap of the semiconductor. Since the dominant recombination process involving two species (electron and hole) radiates photons, it is also called radiative recombination.

The third recombination process is Auger recombination, which involves three charge carriers. In this process, an electron and a hole recombine band-to-band, but they give off their energy to a third particle in the form of kinetic energy. The third carrier usually loses its energy as heat. Auger recombination is only significant in non-equilibrium condition at high excitation densities. In this process, both the energy and momentum must be preserved \[64\]. In fact, Richter et al \[65\] reported that only at \( n > 10^{18} \) the rate equation is related to the carrier density cubic for \( \text{CH}_3\text{NH}_3\text{PbI}_3 \). Since increasing the band gap of semiconductors makes the conservation of momentum more difficult, Auger processes become less important in materials with higher band gaps \[66\].

The contribution of each process depends on many factors including the initial carrier density, the semiconductor’s electronic band structure and the density and energy of trap states within the band gap. Importantly the energy and density of trap states are sample-dependent factors in halide perovskites, and depend on the morphology and fabrication processes of the material \[67\]. Thus it is highly important to distinguish these mechanisms in charge carrier dynamics individually. The decay of charge carrier density \( n \) over time \( t \) is formulated in Equation (1.3): 

\[
\frac{dn(t)}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n
\]

(1.3)

where \( k_1 \) is the recombination rate constant associated with the monomolecular trap-assisted recombination, \( k_2 \) represents the bimolecular radiative recombination rate constant, and \( k_3 \) is the Auger recombination rate constant. As a result, the
total charge recombination rate normalized by carrier density is written as [67, 68]:

\[ R(n, t) = k_3 n^2 + k_2 n + k_1 \]  \hspace{1cm} (1.4)

and by definition, charge carrier lifetime is the inverse of recombination rate:

\[ \tau = \frac{1}{k_3 n^2 + k_2 n + k_1} \]  \hspace{1cm} (1.5)

By knowing the rate constants for each process we can predict the contribution of each to the total recombination rate under a given set of material/device parameters. Recognizing which process has the biggest impact on the total recombination rate helps to define strategies to optimize the contribution of each process, depending on the relevant application of the device and its active semiconductor.

In general, radiative recombination is considered non-detrimental for efficient function of optoelectronic devices, and efforts are focused on maximizing this recombination channel compared to the other pathways [67]. In the direct band gap semiconductors, such as halide perovskites, the radiative recombination originates from the band-to-band relaxation of the free charge carriers. Several different processes can lead to emission in a semiconductor, such as radiative recombination of a free exciton, an electron donor-acceptor pair, or trap-mediated florescence [69]. So far there has been no evidence of other radiative pathway than band-to-band relaxation of free holes and electrons [70]. Therefore we can say that only the recombination coefficient \( k_2 \) represents this radiative process and non-radiative recombination in halide perovskites is mostly from trap-assisted and Auger. However, Richter et al [65] proposed the existence of a non-radiative bimolecular channel. Although the nature of this recombination is unclear, its presence could be speculated from the difference between the recombination coefficients from transient PL and absorption kinetics of \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) thin films.

Non-radiative Auger recombination can be harmful for the performance of devices, but according to both experiments and simulations [65, 67, 71] it does not play a role until carrier densities higher than \((> 10^{18})\) in halide perovskite devices. Therefore, although it can be considered irrelevant for light emitting diodes (LEDs) and photovoltaics under standard sunlight performance conditions [67], it is harmful for applications at high excitation densities like lasing devices or solar cells under concentrators.

The nature, density and energy of traps in perovskites is highly dependant on their fabrication processing. This caused a considerable range of recombination rates, charge carrier lifetime and mobility values being reported in literature for perovskites[72]. For instance, for the most studied hybrid halide perovskite, \( \text{CH}_3\text{NH}_3\text{PbI}_3 \), the PL lifetime varies from nanoseconds to microseconds. It is
suggested that p-type Pb vacancies and n-type methylammonium interstitials form shallow traps near the band edges and cause the PL to quench [58]. Electronphonon coupling has been also suggested as a cause of below gap excitonic and carrier traps formed in halide perovskites [73].

The nature of perovskites as a mechanically soft and chemically less stable semiconductor as compared to the classical inorganic ones, as well as their low energy of trap formation, makes the defect density and states to be sample preparation-dependent [74]. Therefore the study of the defects in perovskites is a complex issue, depending on several factors such as processing temperature and atmosphere, the ratio and age of the initial components, the duration of process, the time between preparation and performance, and even the measurement conditions like humidity and atmosphere. All these factors can decrease or enhance the defect densities and consequently the recombination rates. Moreover, grain boundaries are a source of defects in the polycrystalline film, therefore lower defect density is expected for single crystalline perovskites. Experimental studies [75, 76] estimated small density of traps for single crystals of CH$_3$NH$_3$PbI$_3$ (≈ $10^{10}$ - $10^{11}$ cm$^{-3}$) and CH$_3$NH$_3$PbBr$_3$ (≈ $10^9$) close to the valance (≈ 0.1 eV) and conduction band (≈ 0.2 eV), matching with the predictions from DFT simulations [77]. These findings indicate the superior performance the single-crystalline perovskite devices may have over polycrystalline thin films.

Non-radiative recombination affects the performance of optoelectronic devices in different ways. For instance, in solar cells it causes the charge carriers to decay rapidly, before they reach the electrodes to be collected and contribute to the current. The non-radiative recombination also lowers the voltage of the device at open circuit ($V_{oc}$) from $V_{oc}^{rad}$ according to Equation (1.6) [78, 79], assuming that we have perfect contacts, i.e. the quasi-Fermi level splitting is the same as the extracted device $V_{oc}$.

$$V_{oc} = V_{oc}^{rad} + \frac{k_B T}{q} \ln(\eta_{ext}) \quad (1.6)$$

where $V_{oc}^{rad}$ is the $V_{oc}$ at the radiative limit, $k_B$ is the Boltzmann’s constant and $T$ is the temperature and $q$ is the electron charge. $\eta_{ext}$ is the external quantum efficiency given by:

$$\eta_{ext} = \frac{k_2 n^2}{k_3 n^3 + k_2 n^2 + k_1 n} \quad (1.7)$$

Equation (1.6) and Equation (1.7) show that increasing the non-radiative recombination channels reduces the radiative efficiency and results in a reduced solar cell $V_{oc}$. Therefore achieving highly-efficient solar cells requires strategies to reduce the bulk and surface trap state densities through optimizing processing conditions and passivating the surface or grain boundaries. In light emitting appli-
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cations, the high performance of the device also relies on the high radiative efficiency and minimizing the non-radiative recombination pathways according to Equation (1.7). The recombination processes are highly dependent on carrier concentration (Equation (1.4)). [80, 81]. In lasing applications where the carrier densities are considerably higher, the effect of Auger recombination becomes more dominant. Halide perovskites have Auger recombination rate coefficients ≈25 times higher than GaAs [82], therefore halide perovskite-based lasers may suffer more dramatically from non-radiative Auger channels. Since Auger recombination is based on the simultaneous energy and momentum conservation, it strongly depends on the electronic band structure. Tailoring band structure by proper compositional changes in a way to avoid additional bands, for example split-off bands from spin-orbit coupling, is important for designing efficient devices at high injection levels [72].

1.4 Halide perovskites in optoelectronic applications

Halide perovskites as direct band gap solution-processed semiconductors are efficiently applied to many applications from solar energy conversion [83] and storage [84] to light emission [85, 86] and detection[87, 88]. They behave in many ways like more traditional direct band gap inorganic semiconductors with their long carrier diffusion length and high charge carrier mobility [68]. However, their low-temperature solution-based processing (below 200°C) is analogous to organic semiconductors, making them a potential candidate for cost-effective fabrication of flexible, semi-transparent, colorful thin-film and low-weight devices [84]. Here we give an overview of advances in halide perovskite devices, mainly solar cells, light emitting devices (LEDs and lasers) and photodetectors (PD).

As mentioned in Section 1.1, in the early perovskite-based solar cells, the hybrid halide perovskites were employed as light absorber in liquid electrolyte DSSCs because of their high absorption coefficient \(1.5 \times 10^4 \text{ cm}^{-1}\) at 550 nm compared to the conventional dye \(1.5 \times 10^3 \text{ cm}^{-1}\) for the Ruthenium based organic dye N719 at 540 nm) and broad absorption spectrum. In these devices, CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)NH\(_3\)PbBr\(_3\) nanocrystals were deposited on mesoporous TiO\(_2\) instead of the organic dye. The PCE of these early devices were 3.8% for CH\(_3\)NH\(_3\)PbI\(_3\) and 3.1% for CH\(_3\)NH\(_3\)PbBr\(_3\) based solar cells. Optimizing perovskite precursor solution and electrolyte composition later enhanced the PCE to 6.5% [89]. Although these efficiencies showed the potential of halide perovskites for implementation in photovoltaics, the stability of the devices were low. The perovskites in the liquid electrolyte lasted only about 10 minutes before decomposition. Replacement of the electrolyte with spiro-MeOTAD (2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) in the solid-state DSSC structure increased both the perfor-
1.4 Halide perovskites in optoelectronic applications

mance (PCE 9.7%) and stability [90]. Further improvement to above 12% efficiencies was also achieved by employing mixed halide perovskite CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ for its better stability when processing in air and under light exposure [21, 91, 92].

Within the last years, the architecture of perovskite-based photovoltaic devices developed from DSSC to thin film planar heterojunction (See Figure 1.4). In a conventional DSSC, the sensitizing dye coats a wide band gap semiconductor (like TiO$_2$) and absorbs the photon which consequently generates an electron-hole pair. The electrons are transported to the electrode by transferring to the conduction band of the TiO$_2$, leaving the dye in oxidized state. Simultaneously an electrolyte reduces the oxidized dye to its neutral state and transports the holes to the other electrode. This mechanism is different than conventional inorganic solar cells with \( p-n \) junction architecture [93]. Due to the higher dielectric constant of inorganic semiconductors, the electron-hole pairs are generated, separated and transported directly within the semiconductor. When the mesoporous n-type TiO$_2$ in the perovskite-based solar cell was replaced with the insulating Al$_2$O$_3$ scaffold [21], it was observed that the open circuit voltage (\( V_{OC} \)) and therefore the efficiency was improved. Moreover, transient absorption spectroscopy [92] showed the charge separation is absent in both perovskite/TiO$_2$ and perovskite/Al$_2$O$_3$ interfaces. These reports demonstrated that perovskite itself can sufficiently transport both electrons and holes and enables charge collection in a planar heterojunction, similar to inorganic semiconductors. This was a breakthrough in this field which led to a split of perovskite solar cells from conventional DSSCs and proved the high potential of perovskite solar cells beyond laboratory demonstrations. Today, the international contribution to the progress of this field resulted in the record efficiency of 22.1% in photovoltaic devices. [20]

Despite the high efficiency and relatively simple fabrication of halide perovskite solar cells, several fundamental issues such as performance instability and durability have to be improved. Perovskites in nature consist of ions and evidence of ionic conductivity was reported in inorganic oxide and halide perovskites already many years ago [94, 95]. In hybrid halide perovskites also conduction of ions, known as ionic migration, is proposed to be relevant to the long-term device issues such as degradation[96], and short-term performance issues such as slow response time and hysteresis in current-voltage (I-V) curves [84, 97, 98]. I-V measurement is the typical method to determine the photovoltaic characteristics of solar cells by sweeping the voltage from short circuit to open circuit and recording the current response. In most solar cells, such as Si and organic photovoltaic, the I-V curve does not depend on the direction of the scan, if it is not done too fast [93]. A mismatch between the I-V curves of a perovskite solar cell in forward direction scan (from short circuit to open circuit) and reverse scan is reported since the early stages of perovskite solar cells development [98]. This effect is known as hysteresis. Apart
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Figure 1.4: Evolution of perovskite solar cells from DSSC to planar heterojunction structure a) DSSC structure, with perovskites coating a porous wide band gap semiconductor (like TiO$_2$). The perovskite here serves only as an absorber, while TiO$_2$ transports electrons and a liquid or solid electrolyte transports holes to the respective electrodes. b) In meso-superstructure architecture, perovskite coats a mesoporous metal oxide scaffold. The metal oxide can be a wide band gap semiconductor, or an insulating oxide like Al$_2$O$_3$ which only has a role as a scaffold. Perovskite is capable of not only absorbing light, but also transporting charge carriers. c) The planar structure is realized with a thin film of perovskite sandwiched between electrodes, or with extra charge transport layers, but without a metal oxide scaffold.

from ionic migration, ferroelectricity and charge carrier trapping in perovskites have been also proposed as a mechanism behind hysteresis [4]. Ferroelectricity was initially suggested because of the observed ferroelectric behavior in some oxide perovskite compounds such as BiFeO$_3$ and BaTiO$_3$. Although some early studies hypothesized the rotation of organic cations in hybrid halide perovskites could be responsible for ferroelectricity [99] later more detailed simulations and theoretical work disproved that [100]. Another hypothesis for the cause of hysteresis is charge carrier trapping, which was proposed that occurs due to the migration of mobile ions [101] or the interaction of photogenerated charges with the lattice forming deep trap states, known as small polarons [102]. It is also possible that a combination of all mentioned factors are involved in device-related issues or they are inter-related, but how much each factor is involved is still under debate. Whether the ionic migration can be prevented by tuning processing conditions, or if it can be utilized effectively in the design of novel optoelectronic devices beyond photovoltaics, such as memresistors and switchable diodes, remains as an open question in this field. [103]

Application of direct band-gap perovskite semiconductors in light emission devices (such as LEDs, lasers and light-emitting field effect transistors) has been also widely examined [80, 104, 105]. According to detailed balance in the Shockley-Queisser (SQ) limit [106], when only the radiative bimolecular recombination is considered, an ideal light absorber is an ideal LED as well. The tuning of the band gap by
mixing and substitution of the ions in the perovskite makes it possible to access the full visible light color spectrum for light emission applications. The narrow emission spectra (full width at half maximum ≤20nm) [107] of halide perovskites gives them high color purity. These special emission characteristics, in addition to their high radiative recombination rates, long carrier mobility, and defect tolerance [103] attracts many scientists to study halide perovskites for colorful solid-state lighting [85, 86, 108, 109]. The light emission capability of perovskites, especially their 2-D form, was demonstrated in the 1990s, even before their emergence in photovoltaics [110–112]. However, these early perovskite-based electroluminescence devices were only applicable upon charge injection at very low temperatures. Soon during the first years of development of perovskite solar cells, the incorporation of perovskite nanoparticle emitters in a host (alumina) has been realized [113]. A couple of years after, Tan et al [114] demonstrated green, red and infra-red LEDs with mixed halide hybrid perovskites thin films (CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$ and CH$_3$NH$_3$PbI$_{3−x}$Br$_x$). The broad spectral tunability of perovskites led to the first demonstration of white light emission (blue, green, red) by blending perovskite nanocrystals [115] and perovskite CsPbX$_3$ quantum dots [116] in a polymer host. So far, a lot of efforts have been put together to increase external quantum efficiency of perovskite LEDs up to 3.5% in the near infrared [117] and 8.5% in the green [104], through improving the hole and electron blocking interlayers [117–121] and perovskite film uniformity [104, 122]. Although these efficiencies have improved since the early demonstrations of perovskite LEDs, they are still below those of the well-established organic and colloidal quantum dot LEDs [40]. The main reason is the dominance of trap-assisted non-radiative recombination of carriers at the normal LED carrier injection densities [85]. Thus, further efficiency improvement towards commercialization of perovskite LEDs should be focused on decreasing the monomolecular recombination through methods such as surface passivation, confinement of the injected carrier within perovskite nanograins [104] and synthesis of trap-free perovskite quantum dots [116], as well as improving carrier-selective injection layers [109].

Apart from applications in LEDs, halide perovskites are considered as potential candidates for low-cost solid-state lasers since the demonstration of amplified spontaneous emission of CH$_3$NH$_3$PbI$_3$ films at room temperature [43]. The optically pumped lasing of halide perovskites has been presented both in the polycrystalline thin films [80] and single crystal micro and nanostructures, such as nanowires [123], microdisks [124] and nanoplatelets [125]. Realizing electrically injected perovskite lasers, suitable for commercialization of lasing devices, still remains as a challenge in this field [40].

Halide perovskites show also remarkable potentials in a new generation of low-cost light detection devices applicable in several areas such as imaging and opti-
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cal communication due to their solution processability, high photoconductivity, wide absorption spectral tunability and large charge carrier mobility [87, 88]. The direct band gap nature of perovskites potentially can bring a higher performance for perovskite PDs in comparison to the common Si ones [88]. Following the first demonstration of CH$_3$NH$_3$PbI$_3$ thin film photodetectors, perovskite light detection devices (including photodiodes, photoconductors and phototransistors) with high responsivity ($\geq 10^4 \, A/W$) [126, 127] and detectivity ($\geq 10^{14}$) [128, 129], large linear dynamic range ($\leq 150 dB$) [127, 130], low noise equivalent power ($\leq 50 fW Hz^{-1/2}$) [131, 132] and small response time ($\leq 1 \, ns$) [133, 134] have been realized. Especially, improved crystallinity of perovskites and interfacial engineering have led to low dark current in the thin film based devices [135–137]. Besides the perovskite thin film photodetectors with standard vertical and lateral device configuration [88], PDs based on bulk single crystals and nanostructures (nanosheets and nanowires) have been successfully demonstrated [87]. The perovskite optoelectronic devices had an unprecedented progress in many performance aspects to date, however their further commercialization depends tightly on solving issues like long-term stability of both the material and the device, and the toxicity of lead. A full understanding of the degradation mechanism upon exposure to moisture, light, heat and electric field is required to design long lasting devices. Exploring an alternative divalent cation to replace the toxic lead while maintaining the high efficiency of devices, or offering well-established protocols for recycling the lead without environmental damage are the perspectives for the future advances in this field.

1.5 Perovskites single crystals and nanostructures

The development of the halide perovskites for optoelectronics has not been only devoted to the thin films, but also single crystals and various nanostructures of this class of semiconductors. The monocrystalline perovskites benefit from the lack of grain boundaries and low defect density compared to the polycrystalline perovskite films [138, 139]. In addition to the superior properties like longer carrier diffusion length and lifetime [76, 140], perovskite single crystals are an ideal platform to study the intrinsic photophysical properties [141–144] and crystallographic-dependent characteristics such as facet-dependent degradation [145]. The first demonstrations of the organic-inorganic halide perovskites by Weber [11, 12] was on the single crystals grown from solution temperature lowering - a classical chemistry method to make large single crystals. During the emergence of the halide perovskite field in the past few years, this method (also known as seeded solution growth [132, 140, 146, 147]) along with others, such as inverse temperature [143, 148–152] and anti-solvent vapor assisted [76, 144, 153] crystallization has been revisited to grow
bulk millimeter to centimeter size perovskite single crystals. Although these crystal sizes are suitable for laboratory investigations, methods such as Czochralski and Bridgmann [154, 155], which are common for making wafers of Si and other semiconductor crystals, are not fully developed for halide perovskites. This could be due to the high vapor pressure and instability of organic compounds. Although Stoumpos et al [156] fabricated an all inorganic CsPbBr$_3$ single crystal ingot with the Bridgmann method, there is a lot of room for development of large halide perovskite single crystal growth methods. In addition to the bulk crystals, a few recent studies reported large-area single crystal film growth with innovative methods such as cavitation-triggered asymmetrical crystallization [157], modified inverse temperature crystallization [158, 159], space-confined solution-processed strategy for on-substrate growth [160] and wafer-sized geometrically confined lateral crystal growth [161]. So far, the application of bulk single crystal perovskites in highly efficient devices has been limited to the light detection devices [132, 146, 150, 152], due to the unfavorable thickness of them. Incorporation of single crystal thin films into devices such as solar cells and LEDs will be a breakthrough in this field. Decreasing the dimensions of the perovskite semiconductors tunes their optical band gap further via quantum-size effect. Moreover, nanomaterials can be used for studying the dimension-dependent properties (for example surface effects) as well as building blocks for future optoelectronic devices. Hence, the synthesis and application of various low-dimensional perovskite structures have been investigated extensively in the literature [162], as schematically shown in Figure 1.5. A wide variety of nanostructures are reported in the literature such as 0-D quantum dots and nanoparticles [46, 163–166], 1-D nanowires and nanorods [167–172] and ultrathin 2-D nanosheets and nanoplates [173–177]. Their application is demonstrated in nano-scale devices including optically pumped lasers [45, 123, 178–180], waveguides [181], whispering-gallery-mode nanocavity [125] and also in large-scale devices such as solar cells [170], LEDs [171], photodetectors [182] and field-effect transistors [168] based on nanowire arrays, or solar cells [183–185] and LEDs [46, 115, 186–188] based on quantum dots and nanocrystal assemblies.

1.6 Outline of this thesis

The fabrication and characterization of micro- and nanostructured monocristalline halide perovskites with optoelectronic applications in mind forms the core of this thesis. CH$_3$NH$_3$PbBr$_3$ is chosen as a representative of halide perovskites family, because of the ideal cubic structure, longer stability and less sensitivity to preparation and characterization in the ambient condition. Moreover, CH$_3$NH$_3$PbBr$_3$ has a band gap in the visible, between the high band gap energy of CH$_3$NH$_3$PbCl$_3$ in the UV and the band gap energy of CH$_3$NH$_3$PbI$_3$ in the
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Figure 1.5: Halide perovskite nanostructures’ synthesis and application a) Low-dimensional perovskite nanostructures. b) The application of nanostructures in optoelectronics. Reproduced from Ref. [162] with permission from The Royal Society of Chemistry.

Near-IR.

The first half of this thesis focuses on thin single micro-crystals of CH$_3$NH$_3$PbBr$_3$. Most of the common techniques for making perovskite single crystals from solution suffer from long preparation time and non-ideal bulk size of the crystals, resulting in crystals too thick for most device applications. In chapter two we present a method based on confining the solvent evaporation to fabricate relatively large perovskite crystals with sub-micron thickness from solution. The well-faceted crystals are proven to be monocrystalline using electron back-scatter diffraction (EBSD) microscopy. This method can be generally extended to other perovskites of the halide family. We also introduce a back-contacted electrode configuration to make simple devices for further optoelectrical characterization.

Ionic migration has been proposed as the main mechanism causing short and long-term degradation in halide perovskite devices. In chapter three we aim to study ionic migration and its effect on the performance of back-contacted CH$_3$NH$_3$PbBr$_3$ single crystals. We use the introduced platform to map the elemental composition and photoluminescence in-situ while the crystals are under applied electric field. The direct observation of halide migration in the single crystals is provided with synchrotron-based nanoprobe X-ray fluorescence (nano-XRF) mapping of the perovskite crystal. We show that ionic migration across the crystal changes the optical properties of the crystal locally and causes superior optoelectronic performance where it is bromide-rich.

The second half of this thesis focused on CH$_3$NH$_3$PbBr$_3$ nanowires. In chapter four we describe a template-assisted method to fabricate single crystalline perovskite
nanowires via extrusion through anodized aluminum oxide (AAO) pores. With this method single and arrays of free-standing perovskite nanowires are produced with a simple and fast solution-processed technique. The high optical quality of perovskite single nanowires is tested by measuring photoluminescence quantum yield using the integrating sphere microscopy technique.

In chapter five we study the photophysical properties of perovskite nanowires embedded in an AAO template. The surface plays a major role in non-radiative recombination channels for charge carriers. In this chapter first we investigate the dynamics of excited states using transient photoluminescence spectroscopy. Then we provide a model to relate the charge carriers’ lifetime to the surface to volume ratio of nanowires with various diameters. Using this model, we quantify the surface recombination velocity at the perovskite/alumina interface to understand the role of alumina passivation on the surface of perovskite nanowires.