
Investigating and Improving the Electronic Properties of Perovskite Single Crystals



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Abstract

The aim of the work presented in this thesis is to advance the understanding of the physics underpinning metal halide perovskite single crystals, both in terms of the characterisation of its electronic properties and techniques to improve stability. This study goes on to present a unique mechanism, revealing a new A-site lead halide perovskite, that is also capable of delivering stable high-efficiency photovoltaic cells.

Despite being a young technology, perovskites as material for photophysics and opto-electronic purposes has seen an unparalleled rise in the research community. Results indicate that perovskite-based solar cells provide a step change in performance, compared with older and more established techniques. Their high efficiency, in combination with the ability to process perovskites inexpensively, make perovskite-based cells a new hope in the fight against climate change.

In recent works, electrical characterisation techniques are liberally being applied within the field of perovskite photovoltaics to extract 'key figures of merits' such as trap site density and mobility. However, conventional semiconductor physics do not apply to perovskite-based devices due to the mixed ionic nature of these materials. Therefore, the results from electrical characterisation of perovskites that exemplify the remarkable properties of these materials generate misleading results.

For the development of perovskite-based electronic devices, accurate characterisation of the material's fundamental properties - such as trap and ion density, charge carrier density and mobility value - is of great importance. Therefore, this work initially focuses on investigating the 'space-charge limited current' methodology - a technique that probes the extraction of current as a function of applied bias, through a combination of experimentation and modelling, notably with consideration of the mobile ions which are present in perovskites. Due to inevitable defects associated with grains, grain boundaries and surface interfaces in polycrystalline perovskites, this

work focuses on macroscopic single crystal perovskites, to be able to distinguish the bulk surface properties, and focus on intrinsic key quantities of these materials. This work introduces a new property measurement methodology and analysis. With the proposed numerical modelling, the new method highlights the complexity of the charge transport in the material and provides detailed insights into the fundamental electronic characteristics of perovskite single crystals.

Another grand challenge is the long-term stability of perovskite-based devices. Therefore, the final part of this thesis focuses on understanding the use of an additive to enhance the stability of perovskite single crystals from several hours to over a year. By conducting a comprehensive characterisation of both electronic and material properties, with and without the additive, this study shows a unique mechanism, and reveals the existence of a new mixed A-site perovskite that enables highly stable and efficient photovoltaic devices.

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*The important thing is not to stop questioning.
Curiosity has its own reason for existing.*

Albert Einstein, Life magazine, May 2, 1955

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List of Publications and Conference Presentations

0.1 Publications

1. E.A. Duijnste^e, J.M. Ball, V.M. Le Corre, L.J.A. Koster^{*}, H.J. Snaith^{*}, J. Lim^{*}, Toward Understanding Space-Charge Limited Current Measurements on Metal Halide Perovskites, *ACS Energy Letters*, 5, 376-384, 2020.
2. E.A. Duijnste^e, V.M. Le Corre, M.B. Johnston, L.J.A. Koster^{*}, J. Lim^{*} H.J. Snaith^{*}, Understanding Dark Current-Voltage Characteristics in Metal-Halide Perovskite Single Crystals, *Physical Review Applied*, 15, 014006-1 - 014006-7, 2021.
3. E.A. Duijnste^e, B. Gallant, P. Holzhey, S. Collavini, B. Sturdza, H. C. Sansom, J. Smith, M. J. Gutmann, S. Saha, M. Gedda, M. I. Nugraha, M. Kober-Czerny, C. Xia, A. D. Wright, S. Seo, S. Zhou, A. J. Ramadan, J. Lim, T. D. Anthopoulos, M. R. Filip, M. B. Johnston^{*}, R. Nicholas^{*}, J. L. Delgado^{*}, H. J. Snaith^{*}, Revealing a new formamidinium-based lead triiodide perovskite derived from chemical degradation of precursor solutions, manuscript in preparation for submission to *Nature Chemistry*, 2022.

0.2. Conference Presentations

4. V.M. Le Corre*, E.A. Duijnste^e, O. El Tambouli, James M. Ball, H.J. Snaith, J. Lim, L.J.A. Koster*, Revealing Charge Carrier Mobility and Defect Densities in Metal Halide Perovskites via Space-Charge-Limited Current Measurements, *ACS Energy Letters*. 6. 1087-1094, 2021.

5. J. Lim, M. Kober-Czerny, Y.H. Lin, J.M. Ball, N.Sakai, E.A. Duijnste^e, M.J. Hong, J.G. Labram, B.W Wenger, H.J. Snaith*, Long-range Charge Carrier Mobility in Metal Halide Perovskite Thin-films and Single Crystals via Transient Photo-conductivity, *Nature Communications*. 13. 1-9, 2022.

6. W. Wang, P. Holzhey, Q. Zhang, S. Zhou, E.A. Duijnste^e, C. Chiang, Y. Zhang, C. Wu, H.J. Snaith*, S. Feng*, Water- and Heat-activated Dynamically Evolving Passivation for Perovskite Photovoltaics, manuscript under submission in *Science*, 2022.

7. B. Sturdza, E.A. Duijnste^e, B. Gallant, P. Holzhey, H.J. Snaith, R. Nicholas, Direct Observation of Phase Transitions between Delta and Alpha Phases of FAPbI_3 via Defocussed Raman Spectroscopy, manuscript in preparation, 2022

0.2 Conference Presentations

1. Ionic versus Electronic Conductivity in Single Crystal Perovskites, Oral Presentation, MRS Spring Meeting, May 2019, Nice, France.

2. Insights on Charge Carrier Transport in Perovskite Single Crystals via Pulsed-voltage Space-charge Limited Current Measurements, Oral Presentation, MRS Spring Meeting, April 2020, Phoenix, United States.

3. Understanding the Role of Additives for Stable and High Quality α -Phase FAPbI_3 Perovskite Single Crystals, Oral Presentation, Pacifichem, December 2021, Honolulu, Hawaii.

List of Abbreviations

AFM	atomic force microscopy
CB	conduction band
DOS	density of states
EA	electron affinity
FWHM	full-width-half-maximum
IP	ionization potential
JV	current-density voltage
MG	Mott-Gurney
NMR	nuclear magnetic resonance
PCE	power conversion efficiency
PL	photoluminescence
PV-SCLC	pulsed-voltage space-charge limited current
P-XRD	powder x-ray diffraction
SC	single crystal
SCLC	space-charge limited current
SEM	scanning electron microscope

SXD	single crystal diffraction
TPC	transient photoconductivity
TRPL	time-resolved photoluminescence
VB	valence band
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

CHAPTER 1

Introduction

1.1 The Climate

Throughout history, the Earth has always experienced climate changes, ranging from ice ages to warmer periods. These inevitable cycles are highly dependent on the atmosphere's composition and have occurred as a consequence of natural transformations. The end of the last ice age, about 7000 years ago, marked the beginning of human civilisation, and thereby the starting point of modern climate era. The increase in global population, rapid surge of industrialisation, and subsequent increased energy demands, have caused the most destructive climate change in recorded history, and resulted in extensive quantities of greenhouse gases in the atmosphere - as exemplified by the CO₂ levels in figure 1.1.

Since the industrial revolution our society primarily has relied on fossil fuels to face the surging energy demand. This is driven by the low fossil fuel prices, a powerful and sluggish industry behind them and their particularly high energy density. However, their

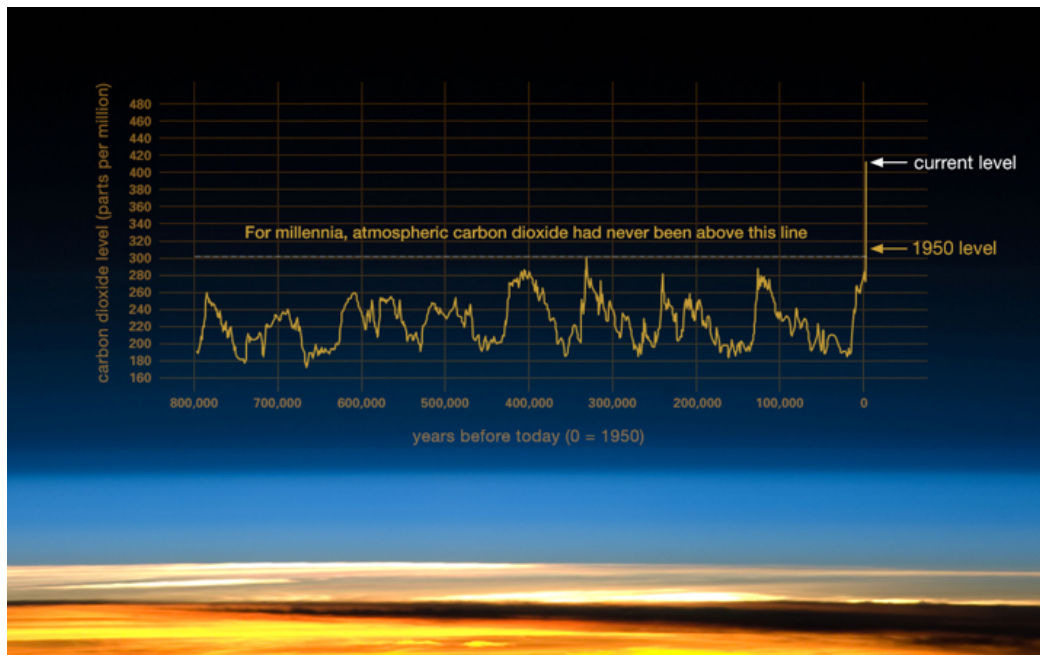


Figure 1.1: Global CO₂ concentration in the atmosphere. (Copyright NASA Goddard Institute for Space Studies).

supply is dwindling and the unavoidable greenhouse gas emissions due to combustion of fossil fuels hasten atmospheric changes. It is now generally accepted within both the scientific community¹ and the public that the abrupt emissions of CO₂, due to human activity, have led to a rise in the average surface temperature on Earth, as depicted in figure 1.2.² In recent years, our planet has started to experience a record number of extreme climate events such as melting glaciers and pole caps, rising sea levels, dying coral reefs, and storms that leave behind unrecognisable cities.^{3,4} While natural climate change seems inevitable, the current rate of greenhouse gas emission is causing the climate on Earth to change 170 times faster than natural forces,⁵ and arguably humans have never influenced the environment of this planet more. In order to reverse or mitigate the evolution of the global climate, human society is urged to turn towards clean and renewable energy sources.

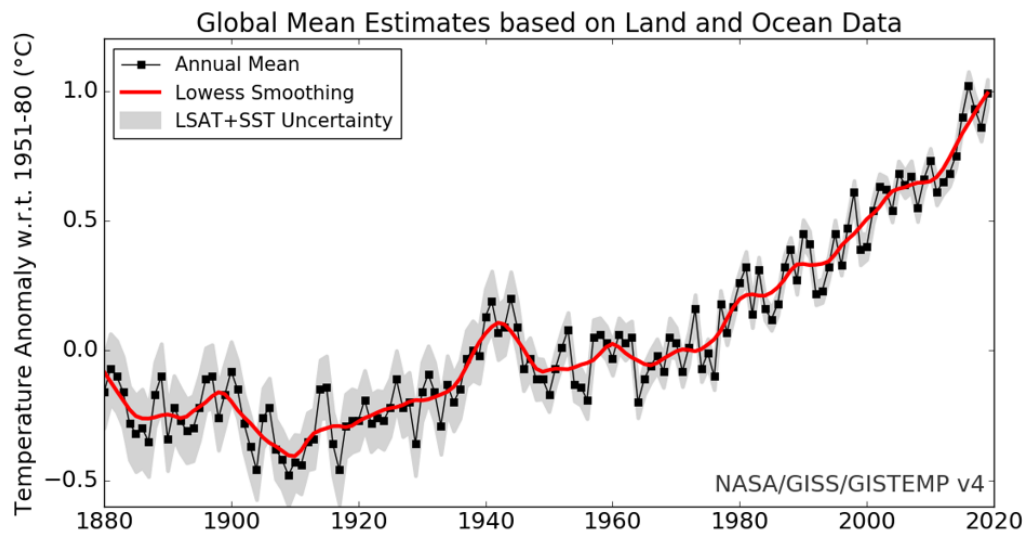


Figure 1.2: Land-ocean temperature index, 1880 to present, with base period 1951-1980. The solid black line is the global annual mean and the solid red line is the five-year lowess smooth. The grey shading represents the total (LSAT and SST) annual uncertainty at a 95% confidence interval. (Copyright NASA Goddard Institute for Space Studies).

1.2 Renewable Energy

The biggest milestones of climate change policy took place at the 2015 and 2021 United Nations Climate Change Conference (COP) in Paris and Glasgow, where 195 countries signed an agreement to do their best to keep global warming well below 2°C, end and reverse deforestation, and cut methane emissions by 30% by the year 2030.

Since these conferences, consequence-taking policies are appearing. Many of them involve the creation of financial incentives for developing, constructing and operating renewable energy producing systems, as well as carbon taxes against the use of fossil-based technologies. Renewables are the fastest growing source of energy, and the energy production has gone up year on year, with sunlight, wind, geothermal heat, waves and rain being the most abundant sources.

1.3 Solar Energy

Solar energy, which currently has the highest growth rate,⁶ plays an extremely interesting role, as a high irradiance of sunlight is well distributed across the planet, and especially in countries with dense population.⁷ To meet the global energy demand in 2050 (estimated as ca. 25 TW),⁷ only 1% of the incident solar energy on the Earth's surface has to be converted with 10% efficient photovoltaic devices.

A key factor that has inhibited the growth of solar energy was its high price relative to fossil fuels. However, the price of silicon based solar panels has dropped tremendously over the past years due to improvement in efficiency, economies of scale and improved production yields, insofar as the solar energy is cheaper than energy from the grid in many places. Nonetheless, due to the high capital expenditure cost for production equipment, the price of the solar modules is not sufficiently low for solar energy to be competitive in all regions without financial incentives from governments. Additionally, conventional technologies like silicon solar cells are not carbon-neutral due to heavy manufacturing processes. While incentives from government would urge the adoption of solar power, further scientific innovations that push the technology to become cheaper, more effective and more sustainable (by using earth-abundant materials whilst limiting CO₂ emission during the fabrication process), are required to make a significant contribution to limit further climate change.

1.3.1 Perovskite Solar Cells

Nowadays, hundreds of researchers worldwide turn their attention towards perovskite solar cells, which created tremendous enthusiasm in the photovoltaic community due to the energy conversion efficiency boosts of over 25% in a just a decade of research.^{8–11} This incredibly quick improvement renders perovskites as one of the most exceptional and market-competitive optoelectronic materials for many applications in

photovoltaic devices,^{8,11} including but not limited to: field-effect transistors,¹² light emitting diodes,¹³ photodetectors,¹⁴ and lasers.^{15,16} The outstanding performances of perovskites derive from the intrinsic properties they possess. Their extreme attributes include an adjustable spectral absorption range,¹⁷ a high carrier mobility, long carrier lifetime,¹⁸ and high diffusion length. This, together with their low processing costs, ease of fabrication and integration possibilities, make perovskites the rising star of new photovoltaic architectures.

Perovskites have often been described as a 'wonder material' due to their almost ideal opto-electronic properties for photovoltaic applications, and are therefore very promising candidates to disrupt the solar technology market and make a significant contribution to limit climate change. Still, many fundamental scientific questions remain to be answered, and issues for mass production need to be overcome, which the work of this thesis aims to contribute towards.

1.4 Aims of this Thesis

The central aim of this thesis is to give a better understanding of the fundamental physics of metal halide perovskites. Two main bottlenecks in perovskite research are tackled: ionic conductivity and stability. Understanding and controlling the properties of perovskites is needed to make this nascent material more competitive with existing materials used in semiconductor physics.

Chapter 2 provides a concise overview of the physics and materials concepts essential to this thesis. It begins with a review of core semiconductor physics, introduces charge transport in semiconductors and explains the general working principles of electronic conductivity measurement techniques. Then, perovskites are introduced. Particular attention is given to how perovskites can differ from conventional semiconductors due to their mixed electronic and ionic conductivity, and to the instability

issue of perovskites. Next, it is explained how perovskite single crystals are ideal to study the intrinsic properties of the material. This chapter also lays out the underlying device physics that is used for the simulation studies in chapter 4 and chapter 5.

Chapter 3 provides an overview of the methods used for the work in this thesis. The materials and processes for single crystal growth and respective device fabrication are explained. The latter half of the chapter explains the device characterisation techniques used in this body of work.

Next, the thesis presents findings of several investigations, where each chapter includes a detailed introduction and literature review relevant to the investigation, followed by presentation of the results, discussion and summary.

Chapter 4 demystifies the effect of mobile ions in space-charge limited current (SCLC) measurement on metal halide perovskites. SCLC measurements are often used for the identification of important intrinsic properties such as trap density and mobility. This chapter firstly articulates the deficiencies of the SCLC technique. It is shown how ionic conduction can have a significant effect on electronic conductivity during space-charge limited current measurements, and thereby can cause erroneous interpretations and results. Then, a novel pulsed-voltage SCLC (PV-SCLC) measurement is introduced to achieve reproducible current density - voltage (JV) curves without hysteresis. With this modified measurement methodology, a lower bound trap density is calculated via a combination of experimental techniques and computational modelling.

Chapter 5 surrounds a fundamental study on the background carrier density of perovskite single crystals. From a temperature-dependent study using the novel PV-SCLC method introduced in Chapter 4, the background carrier density in MAPbBr₃ and MAPbI₃ single crystals is identified. A combination of this, with theoretical

calculations, exemplifies that the background carrier density in these single crystals is due to different factors such as thermal injection, temperature-dependent mobility and trap and ion density.

Chapter 6 tackles the instability issue of FAPbI_3 under ambient conditions. The chapter describes how, in the presence of the additive MDACl_2 , α - FAPbI_3 single crystals are grown which remain in the stable α -phase for more than a year with vastly improved electronic properties. It is found that MDACl_2 degrades rapidly in solution, and this work postulates that the symbioses of one of the degradation products and FAPbI_3 stabilise each other and offer a unique and previously unknown mechanism. It reveals the existence of a new mixed A-site lead-halide perovskite that is capable of delivering high-efficiency photovoltaic cells with high α -phase stability.

Finally, Chapter 7 provides a summary of the work described here and offers insights for future research directions.

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CHAPTER 2

Fundamentals and Background

This chapter gives an overview of the fundamental concepts that are required to understand the work presented in this thesis. Firstly, the key properties of intrinsic semiconductors are discussed, followed by the theoretical treatment of charge transport through semiconducting devices. Then the analytical description of charge transport in single carrier devices is given. This forms the basis to understand the theory of space-charge limited current measurements, the most used electrical characterisation method in this thesis. For more in depth information on the fundamentals of electronics, the reader should refer to standard textbooks.^{1–4} In the second part of this chapter, the perovskite crystal structure and its fundamental properties are discussed, and the concepts of mobile ions, anomalous hysteresis, and stability, are explained.

The success of recent semiconductor technologies, such as solar cells, light-emitting diodes, transistors and many more, is due to a combination of improved understanding and enhanced processing of well established materials and because of the development of new materials with improved properties and charge transport characteristics.

2.1 Semiconductors

A semiconducting material is neither a good insulator, nor a good conductor, but has great electrical properties upon the addition of heat, voltage or light, making them an essential component of electronic devices by enabling advances in energy conversion, computing, communications, and countless other applications.

2.1.1 Electrons in an Intrinsic Semiconductor

A perfect semiconducting material, called an intrinsic semiconductor, contains no impurities and no (or a very low degree of) energetic disorder. When two atoms are in close proximity, their electron orbitals split and thereby define allowed quantum energy states that an electron can occupy. In a solid with a large number of atoms and periodic crystallinity, these degenerate energy levels are not discrete anymore but rather form a continuum, or band, of allowed energy states, which are separated by energy values much smaller than the thermal energy of ~ 25 meV at room temperature.

2.1.1.1 Energy Bands

In a crystalline material, the electron is subjected to a periodic potential, i.e. the potential repeats itself in space in a practically infinite lattice. In a three-dimensional crystal, this lattice can be characterised by three vectors a_1 , a_2 and a_3 . These vectors define the smallest possible unit cell. In reciprocal or momentum space, a_1 , a_2 and a_3 are translated into reciprocal lattice vectors k_1 , k_2 and k_3 , which define the Brillouin zone. The Brillouin zone is a particular choice of the unit cell in the reciprocal lattice, and describes the electron energy of the band structure of crystals.

According to quantum physics, the electronic states in the material can be mathematically described as electron probability distributions which are represented by a wavefunction (Ψ). The wavefunction is called a Bloch wave, and is defined as a

plane wave representing the wavefunction of an electron in free space, modulated by a periodic function that is related to the crystal lattice. In order to resolve these electronic states, the Schrödinger equation, which is the linear partial differential equation that describes the wavefunction of a quantum-mechanical system, has to be solved. This derivation is out of the scope of this thesis, but can be found in reference².

The solutions of the Schrödinger equation describe the electron energy, E , as a function of the wave vector k . The eigenstate distribution, $E(k)$, is known as the band structure of the crystal. The wave vector k follows $k=n\pi/a$, where a is the distance between atomic planes, and n indicates that the energy distribution repeats itself due to the periodic potential of the crystal. All possible eigenstates of $E(k)$ are confined to wave vectors in the range between $0 < k < \pi/a$ because of the periodicity and symmetry of the crystal. A schematic of eigenstates within a Brillouin zone in one dimension, and its equivalent energetic band diagram, is depicted in figure 2.1.

When the electrons in a semiconductor are in their lowest energy state, i.e. at $T=0$ K, the energy bands are defined as the valence band (VB , the highest energy band which is filled by electrons) and the conduction band (CB , the first available empty band). In a semiconductor, the CB is separated from the VB by the band gap. In this forbidden gap, the Schrödinger equation has no solutions for energies within the band gap at $k=\pm\pi/a$. Therefore, the band gap has no available states and is thus free of electrons. The band gap energy E_g , is the difference between the energy of the conduction band edge E_C , and the valence band edge E_V (see figure 2.1). E_g also corresponds to the minimum amount of energy required to promote an electron from the VB into the CB upon supply of external energy to the semiconductor. When an electron is excited to the CB , a hole, which is an unoccupied state in the VB , is left behind. Holes are treated as quasi-particles with an effective positive charge.

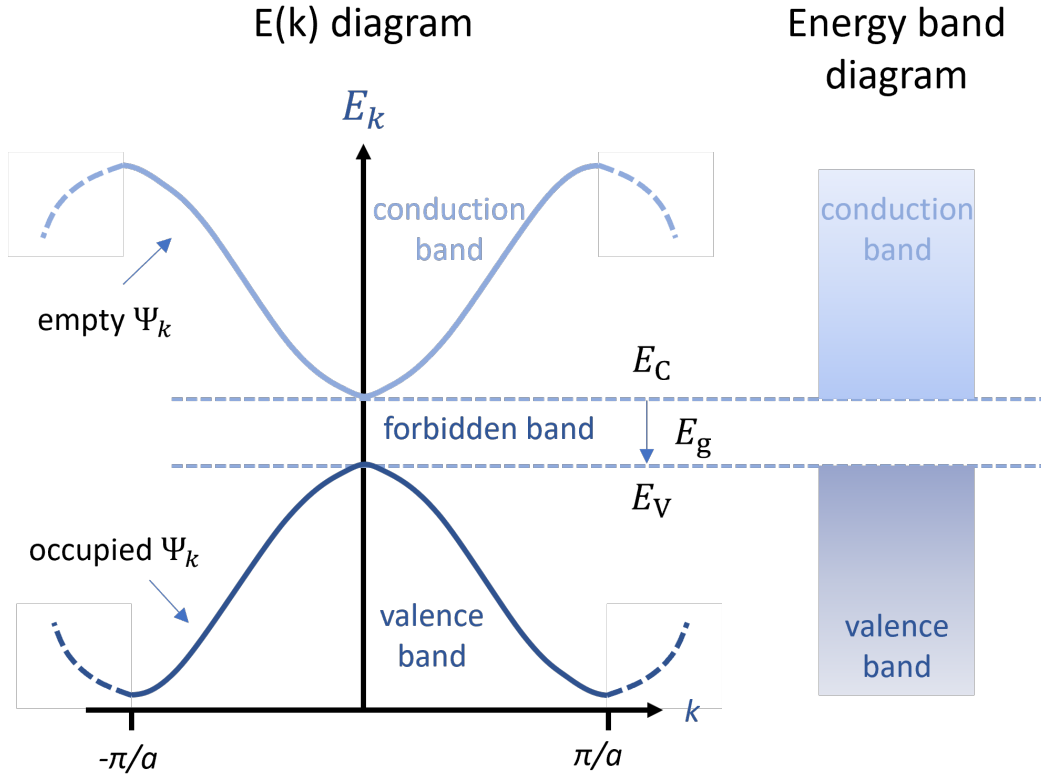


Figure 2.1: Schematic of the $E(k)$ diagram within a Brillouin zone for one lattice direction (left) and the equivalent energetic band diagram (right). The $E(k)$ curve represents the wavefunction and consists of many discrete points, where each one of them corresponds to a possible energy state. Within the band gap, corresponding to the energies between the valence band and the conduction band, the wavefunction has no solutions.

2.1.1.2 Fermi Level

In the band structure theory, the Fermi level, E_F , can be considered to be a hypothetical energy level of an electron such that this electronic energy state has 50% probability of being occupied at thermodynamic equilibrium. In an intrinsic semiconductor, E_F is in the middle of the band gap. The probability of occupancy of an energy level at energy E at temperature T is governed by the Fermi-Dirac distribution function:

$$f(E) = \frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right) + 1}, \quad (2.1)$$

where k_B is the Boltzmann constant.

2.1.1.3 Density of States

Even though the occupation probability is dependent only on energy, the density of states (DOS), which describes the number of states that is occupied by the system at each level of energy, is dependent on both energy and momentum of electrons. However, within the band theory of solids, the movement of particles in a periodic potential can be very different from their motion in vacuum. Therefore, the effective mass (m^*) is introduced. This is a quantity used to simplify band structures by describing the mass of an electron while taking into account the effect of the periodic potential of the electron. It is defined as follows:¹

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2}, \quad (2.2)$$

where $\hbar = h/2\pi$, where h is Planck's constant.

The kinetic energy E of a particle with mass m^* is related to the wave vector k via:

$$E(k) = \frac{\hbar^2 k^2}{2m^*}. \quad (2.3)$$

Providing that

$$\frac{dk}{dE} = \frac{m^*}{\hbar^2 k}, \quad (2.4)$$

$$k = \frac{\sqrt{2m^*E}}{\hbar}, \quad (2.5)$$

and the DOS per unit volume and per unit energy, $g(E)$, equals:

$$g(E) = \frac{1}{a^3} \frac{dN}{dE}, \quad (2.6)$$

where dN/dE is the density per unit energy and is equal to:

$$\frac{dN}{dk} \frac{dk}{dE} = \left(\frac{a}{\pi}\right)^3 \pi k^2 \frac{dk}{dE}. \quad (2.7)$$

After further substitution of equation 2.2, 2.3, 2.4, 2.6 and 2.7, the DOS per unit volume and per unit energy equals:

$$g(E) = \frac{8\pi\sqrt{2}}{h^3} m^{*\frac{3}{2}} \sqrt{E}. \quad (2.8)$$

The DOS for electrons in the conduction band is then given by:

$$g_C(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_C)}}{\pi^2 \hbar^3}, \quad (2.9)$$

and the DOS for holes in the valence band by:

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V - E)}}{\pi^2 \hbar^3}, \quad (2.10)$$

where m_n^* and m_p^* are the respective effective electron and hole masses. A schematic of the three dimensional DOS is represented in Figure 2.2

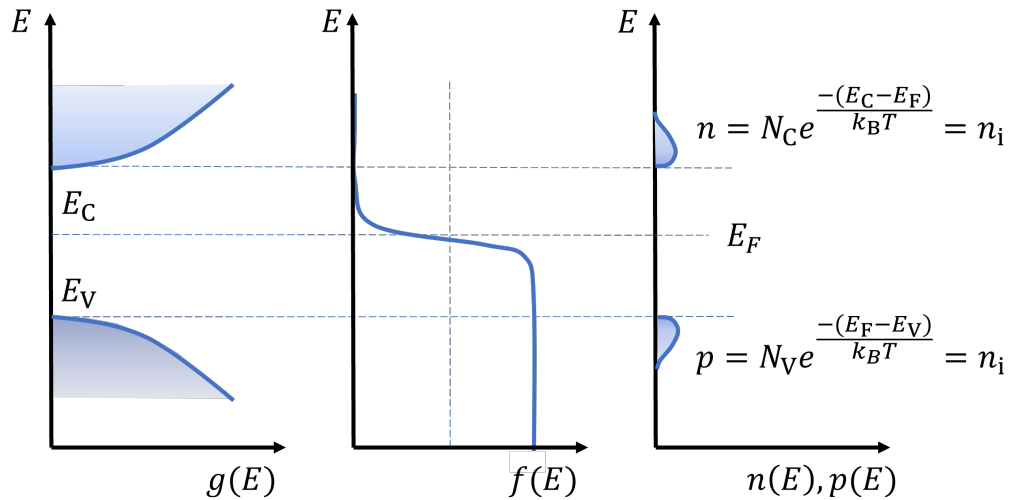


Figure 2.2: Schematic of the density of states for electrons and holes (left), the Fermi-Dirac distribution function (middle) and the respective intrinsic electron and hole densities (right).

2.1.1.4 Charge Carrier Density

The charge carrier density can be calculated from the DOS using the Fermi-Dirac distribution function (equation 2.1) integrated over all possible energies. The electron (n) and hole (p) density are derived as follows:

$$\begin{aligned}
 n &= \int_{E_C}^{\infty} g_C(E) f(E) dE \\
 &= 2 \left(\frac{2\pi m_n^* k_B T}{h^2} \right)^{\frac{3}{2}} \exp \left(-\frac{E_C - E_F}{k_B T} \right) \\
 &= N_C \exp \left(-\frac{E_C - E_F}{k_B T} \right), \tag{2.11}
 \end{aligned}$$

and

$$\begin{aligned}
 p &= \int_{-\infty}^{E_V} g_V(E) [1 - f(E)] dE \\
 &= 2 \left(\frac{2\pi m_p^* k_B T}{h^2} \right)^{\frac{3}{2}} \exp \left(-\frac{E_F - E_V}{k_B T} \right) \\
 &= N_V \exp \left(-\frac{E_F - E_V}{k_B T} \right), \tag{2.12}
 \end{aligned}$$

where N_C and N_V define the effective DOS of the CB and VB , respectively, such that:

$$N_C = 2 \left(\frac{2\pi m_n^* k_B T}{h^2} \right)^{\frac{3}{2}}, \tag{2.13}$$

and

$$N_V = 2 \left(\frac{2\pi m_p^* k_B T}{h^2} \right)^{\frac{3}{2}}. \tag{2.14}$$

2.1. Semiconductors

In an intrinsic semiconductor, the electron density equals the hole density ($n = p$). The law mass of action states that at thermal equilibrium, the product of these two (np) must be a constant which is independent of the Fermi energy, which is defined as the energy of the highest occupied state at 0 K, and is related to the the intrinsic charge carrier density (n_i) as follows:

$$n_i^2 = np = N_C N_V \exp\left(-\frac{E_g}{k_B T}\right). \quad (2.15)$$

From this, an expression for the semiconductors' intrinsic potential energy (E_i), which is equal to the Fermi energy (E_F) of an intrinsic semiconductor, follows:

$$E_i = E_F = \frac{1}{2}(E_C + E_V) - \frac{1}{2}k_B T \ln\left(\frac{N_C}{N_V}\right). \quad (2.16)$$

Whether a material is conducting or not is dependent on the size of the band gap and the position of the Fermi level. A schematic of the band structures of a metal, semiconductor and insulator are depicted in figure 2.3. For electrical conduction to occur, the *CB* must have a certain fraction of energy states filled with mobile electrons, implying that $n > 0$. In a metal, there is an overlap of the *VB* and the *CB* so that at least a fraction of the valence electrons can move freely through the material. In contrast, in an insulator, there is a large forbidden gap (for example $E_g > 4$ eV) between the energies of the valence electrons and the energy at which the electrons can move freely through the material in the *CB*. Semiconductors have a relatively small band gap ($0.5 \text{ eV} < E_g < 3 \text{ eV}$) with the Fermi level in the middle of the band gap, such that there is a non-zero probability for electrons to occupy energy states in the *CB* for $T > 0$ K. Electrons that are excited from the *VB* to the *CB* upon the addition of external energy cause an increase in mobile carrier density.

In terms of the band theory of solids, the electrical conductivity (σ) is thus proportional to the concentration of mobile charge carriers via:

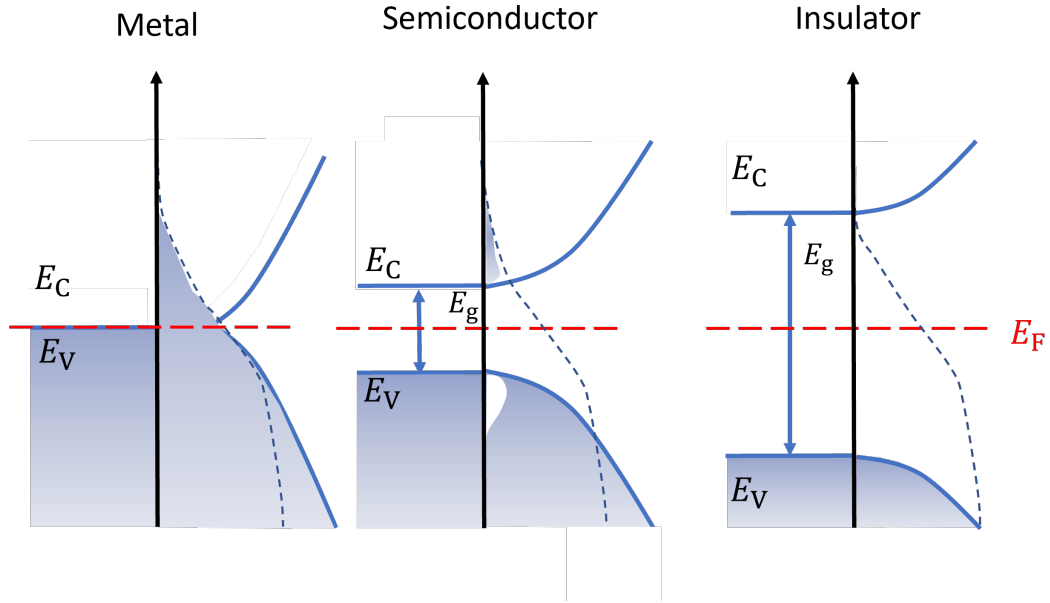


Figure 2.3: Schematic of the energy band diagrams, Fermi-Dirac distribution, density of states and charge carrier concentrations for a metal (left), a semiconductor (middle) and an insulator (right) at thermal equilibrium. In a metal, the Fermi level is in the middle of a continuum of partially filled states, which allows for electrical conduction. An insulator does not conduct free charges as the band gap is too large for electrons to be excited from the valence band into the conduction band. In a semiconductor, the band gap is such that it allows for mobile electrons in the conduction band when additional external energy is supplied to the semiconductor.

$$\sigma = en\mu, \quad (2.17)$$

where n is the carrier density, e is the elementary charge and μ is the charge carrier mobility.

2.1.1.5 Charge-carrier Mobility

Independent on the purpose of opto-electronic devices, their performance always depends on the charge carrier mobility, μ . In the absence of an external field, charge transport is a diffusive process. The mean-square displacement of a charge carrier, $\langle x^2 \rangle$, due to the random motion in the material, can be described as follows: $\langle x^2 \rangle = nDt$, where n is 2, 4, or 6, depending on the dimension of the system, D is the diffusion coefficient and t is time. The mobility of electrons or holes is related to D via the Einstein equation:

$$\mu_{n,p} = \frac{qD}{k_B T}, \quad (2.18)$$

where q is the electron or hole charge. In the absence of an external driving force, there is only a local displacement of the charge around an average position, and so the current across the material is zero.

2.1.1.6 Current Density

In the presence of an external driving force, the charge carriers drift, and the mobility is defined from the carrier velocity v and the electric field F as follows:

$$v = \mu F. \quad (2.19)$$

The drift induces a displacement of the average position, which results in a drift current flow, J_{drift} , that can be described by:

$$J_{\text{drift}} = \rho v = \rho \mu F, \quad (2.20)$$

where ρ is the charge density. A local diffusion current, J_{diff} , that depends on the mobility via the diffusion coefficient, can flow simultaneously if there is a local excess of charge according to:

$$J_{\text{diff}} = qD \frac{d\rho}{dx}. \quad (2.21)$$

The total current is the sum of the drift (equation 2.20) current and the diffusion current (equation 2.21):

$$J = J_{\text{drift}} + J_{\text{diff}} = \rho \mu F - qD \frac{d\rho}{dx}. \quad (2.22)$$

Both the magnitude of the mobility and the magnitude of the carrier density play an important role in the total current flowing through the material. For example, if

the semiconductor contains traps, the overall density of free charge decreases, and the material transport properties are strongly affected. To characterise the material's electrical properties, and work towards limiting losses in semiconductor devices, it is thus essential to probe quantities such as carrier density, trap density and mobility. There exist a number of charge transport characterisation methods such as time-of-flight measurements, Hall bar measurements, and space-charge limited current measurements.

2.1.1.7 Energetic Disorder and Trap States

So far, this chapter has discussed intrinsic semiconductors. However, in real applications, semiconductors rarely behave purely intrinsic as most solution processed materials suffer from poor crystallisation and film formation, and have some degree of disorder or traps. In this case, some adaption to the classical semiconductor theory is required for the understanding charge transport through the material.

Deviation of the degree of material crystallinity results in the creation of energy states within the band gap, called trap states, and charges travelling through the material will preferably occupy the lowest possible energy state. An excited charge carrier can be captured by trap states of different energies, depending on how close the traps are to the band edges. Shallow traps, i.e. the nearest to the band edge, capture carriers that can still be thermally released to the system, while charges that are trapped in deep traps, i.e. traps far from the band edge, cannot be thermally released, and tend to be lost to recombination. The variation in the material's energy landscape thus affects on the charge transport, and the transport and optical properties decrease with increasing energetic disorder.

Imperfections in the material can be caused by structural discontinuity (crystallographic defects) or by another chemical species (impurity) present in the material.

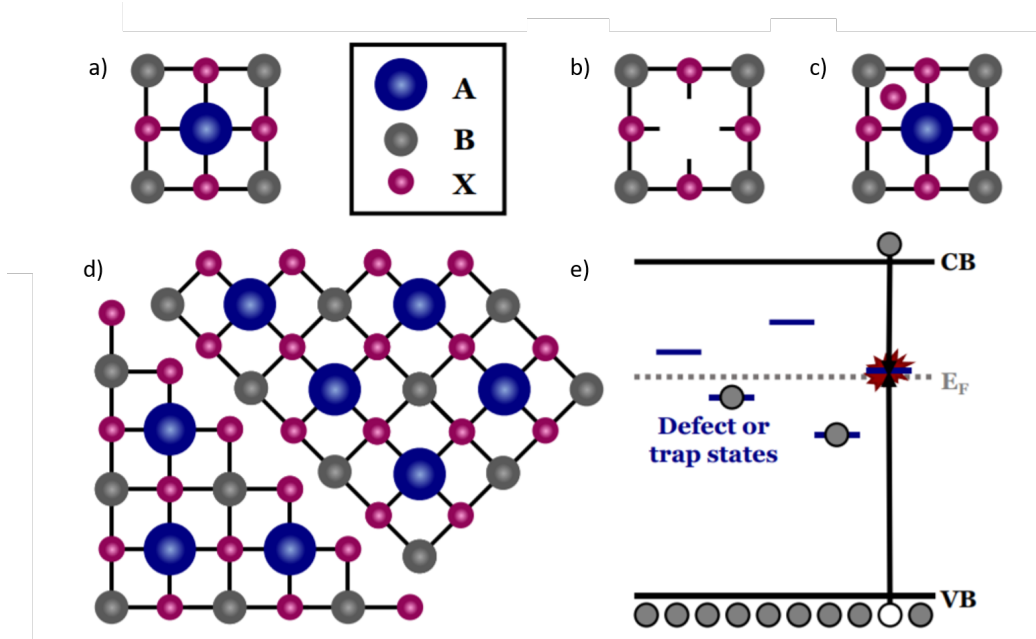


Figure 2.4: Crystallographic defects in the perovskite lattice of A, B, and X ions; a) a perfect lattice; b) a vacancy; c) an interstitial; d) a grain boundary; e) trap states in the middle of the band gap.

Impurities are mostly intentional to dope the material. Crystallographic defects, however, are unintentional and are present in all semiconductors, even when the processing conditions are nearly perfect. These defects include vacancies in the lattice site and ions in interstitial lattice sites, as shown in figure 2.4a-c. We will elaborate more on these type of defects in section 2.2.4. Larger scale structural defects include grain boundaries in polycrystalline thin films, as depicted in figure 2.4d. In figure 2.4e it is schematically illustrated how defects or traps create their own energy levels.

2.1.2 Theoretical Treatment of Charge-Transport in Semiconductors

To study the properties of semiconducting materials, the fundamental physics of charge transport through the material has to be understood. Many current-density voltage (JV) measurements are performed on devices containing only one type of charge carriers (electrons or holes), i.e. single-carrier devices.

2.1.2.1 Single Carrier Devices

To understand the current response of a single-carrier device to an applied electric field, this section discussed the metal/semiconductor interface.

2.1.2.2 Metal/Semiconductor Interface

The energy diagram of the metal/semiconductor interface is depicted in figure 2.5a. χ is the work function, which is a material dependent parameter and is defined as the amount of energy required to release an electron to vacuum. χ_m is the metal work function and indicates the ease with which a metal will react. Generally, the larger the work function, the less reactive the metal. In a metal, it equals the difference in energy between the Fermi level of the metal ($E_{F,m}$) and the vacuum level energy, E_{vac} ($\chi_m = E_{vac} - E_{F,m}$).

A semiconductor is defined by its electron affinity (EA), the ionization potential (IP), the band gap (E_g) and the work function (χ_{sc}). EA is the affinity for the semiconductor to accept an electron and equals the difference between the conduction band energy and the vacuum level energy ($EA = E_{vac} - E_C$). IP is the amount of energy required for an electron to ionise from the valence band to the vacuum and equals the difference between the valence band energy and the vacuum energy level ($IP = E_{vac} - E_V$). χ_{sc} is the semiconductor work function, which equals the difference between the Fermi level of the semiconductor ($E_{F,sc}$) and the vacuum level energy ($\chi_{sc} = E_{vac} - E_{F,sc}$). $E_{F,sc}$ is the Fermi level of the semiconductor and governs the relative concentration between electrons and holes. The Fermi level is valid at any temperature, and is related to the chemical potential of a system of electrons, as defined by the Fermi-Dirac distribution.

When a metal and a semiconductor are in contact, as shown in figure 2.5b, charge will be injected from the metal into the semiconductor until the Fermi levels of both

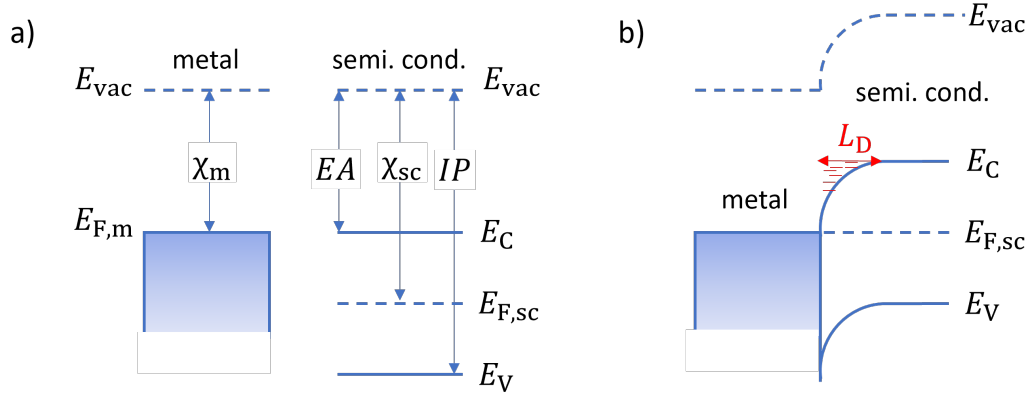


Figure 2.5: Metal/semiconductor band diagram; a) a metal and a semiconductor before they are in contact and the Fermi levels equilibrate; b) metal/semiconductor interface (Ohmic contact) where electrons are injected into the semiconductor near the interface. The depth of the space-charge region at the interface is about equal to the Debye length.

align, and the interface reaches a thermodynamic equilibrium. Therefore, the free charge-carrier density will increase with orders of magnitude compared to the intrinsic carrier density, and a space-charge layer is formed. The depth of this layer is roughly equal to the Debye screening length, and equals:⁵

$$L_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{q^2 n}}, \quad (2.23)$$

where n is the charge-carrier density in the device.

If the work function of the metal and the conduction band edge of the semiconductor are at the same energy, there is an Ohmic contact between the two materials. A non-Ohmic contact is formed when the work function of the metal is in between the Fermi level of the semiconductor and the conduction band edge.¹ If the conduction band edge energy lies lower than the Fermi level of the metal, charge-carriers are injected into the semiconductor until the Fermi levels align. An Ohmic contact is formed, but the effective thickness of the semiconductor will be reduced as the interface of the semiconductor will be highly doped due to charge injection.⁶

For a doped semiconductor, the Fermi level highly depends on the amount of doping in the material. Similar to a metal/intrinsic semiconductor interface, if χ_m is equal to the conduction band edge of the n-type semiconductor, an Ohmic contact is formed, and if χ_m is larger than $E_{\text{vac}} - E_C$ but smaller than χ_{sc} , a non-Ohmic contact is formed. However, in the latter, the injection barrier is often so small that it is called a near-Ohmic contact. If χ_m is larger than χ_{sc} , band bending will result in a Schottky contact.⁶

2.1.2.3 Double-Junction Single Carrier Device

A single-carrier device consists of a semiconducting material sandwiched between two electrodes, and has a metal/semiconductor interface at each side of the semiconductor. The metal work functions are selected to form an Ohmic or non-Ohmic contact, and are such that the transport across the semiconductor is electron or hole selective. It is important to note that if the thickness of the semiconductor is smaller than twice the Debye length, charges are injected from both electrodes and the carrier density is orders of magnitude higher than the intrinsic density over the whole thickness of the semiconductor.⁷

2.1.3 Analytical Description of Charge-Transport through Single-Carrier Devices

Following up on the theoretical treatment of charge transport at the metal/semiconductor interface, this section explains the most common analytical equations (and its limitations) that describe charge transport in single-carrier devices. The space-charge limited current measurement (SCLC) measurement is one of the most common tools for electrical characterisation in semiconductor physics.

2.1.3.1 Space-Charge Limited Current Measurement

The SCLC electrical characterization technique measures the dark JV characteristics of a unipolar device, to study the electron or hole transport and injection properties, without requiring light illumination for the generation of charge carriers.^{1,8-10} Due to the apparent simplicity it has been used extensively in the literature to study organic semiconductors and inorganic and hybrid organic-inorganic metal halide perovskites.¹¹⁻²² One of the main advantages of this technique versus other techniques such as time-of-flight measurements and optical pump terahertz probe photoconductivity, is that the electron and hole mobility and the trap density can be measured independently.^{23,24} Additionally, the device configuration is similar to the 'sandwich structure' used in solar cells and other optoelectronic devices, where the vertical transport is probed.

However, several pitfalls of SCLC analysis are often overlooked and the analysis of SCLC measurements is repeatedly oversimplified. This can lead to erroneous values of extracted parameters, which will be elaborated on in chapter 4 and 5. To fully understand SCLC, this section will discuss the essential theory all the way from the drift-diffusion equation to the pitfalls of the SCLC measurements.

2.1.3.1.1 Slope The JV characteristics extracted from SCLC measurements are commonly plotted on a logarithmic scale. This yields important information about the transport of charges at low voltages which would otherwise be hidden, and is important to examine the slope of the JV curves on a log-log scale. The slope of the JV curve, m , is given by:

$$m(V) = \frac{d\log J}{d\log V}. \quad (2.24)$$

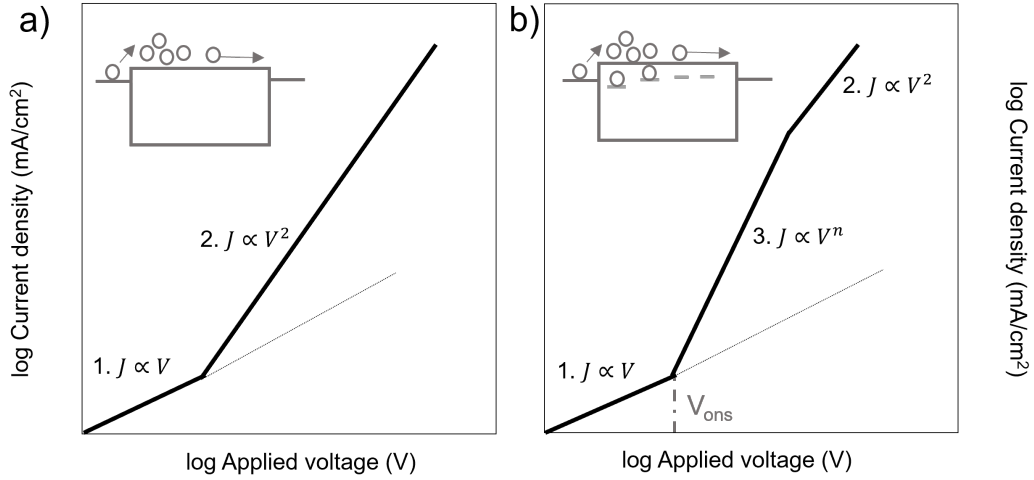


Figure 2.6: Schematic illustration of the principle of the SCLC measurement; a) SCLC behavior for a trap-free semiconductor. Two charge transport regions are visible: (1. $J \propto V$) Ohmic region and (2. $J \propto V^2$) SCLC region; b) SCLC behavior for a semiconductor with trap states. Three charge transport region are visible: (1. $J \propto V$) Ohmic region, (3. $J \propto V^n$, $n > 2$) trap-filling region, and (2. $J \propto V^2$) SCLC region in the absence of trapping.

The slope changes as the transport changes from one regime to another (schematic in figure 2.6), and from the definition of the slope, the current density depends on the power of the voltage by:

$$J \propto V^{m(V)}. \quad (2.25)$$

Conventionally, for the case of unipolar conduction, the JV curve first follows Ohm's law (1. $J \propto V$ in figure 2.6a), where the conductivity is determined by the background carriers.^{7,10} When the injected free carrier concentration exceeds this background charge carrier concentration, the space-charge effect is said to occur, where the current is limited by the build-up of space-charge (2. $J \propto V^2$ in figure 2.6a), and the current follows the Mott-Gurney (MG) law.

2.1.3.1.2 Mott-Gurney Law (Ideal Transport) The MG law is the most commonly used equation for analysing SCLC in the absence of traps, dopants and energetic disorder. It describes drift-only transport through a semiconductor with Ohmic contacts to the electrodes, and is given by:²⁵

$$J = \frac{9}{8} \mu_n \varepsilon_r \varepsilon_0 \frac{V^2}{L^3}, \quad (2.26)$$

where μ_n is the electron mobility, ε_r is the dielectric constant, ε_0 is the permittivity of free space, L is the thickness of the semiconductor and V is the difference between the applied voltage and the built-in voltage. For two Ohmic contacts, the built-in voltage equals zero.

The MG law shows that the drift current is not increasing linearly with the voltage, as would be expected from Ohm's law for charge transport across a metal or highly doped semiconductor. This is not as surprising as it arises from the non-uniform distribution of the large concentration of space-charge in these types of devices. In this regime, the current is said to be limited by the build-up of space charge. This means the limitation of current in a material due to repulsion exerted on electrons that are injected by electrons that are in the active material.

2.1.3.1.3 Derivation of the Mott-Gurney Law The MG law derivation starts from the steady-state drift-diffusion current density equation that was introduced in section 2.1.1.6, but here specified for electrons:

$$J_n = qD \frac{dn(x)}{dx} - qn(x)\mu_n F(x), \quad (2.27)$$

and holes:

$$J_p = -qD \frac{dp(x)}{dx} - qp(x)\mu_p F(x), \quad (2.28)$$

where D is the Einstein diffusion coefficient, $n(x)$ and $p(x)$ are the respective electron and hole density as a function of spatial position inside the semiconductor, x . μ_n is the electron mobility, μ_p is the hole mobility and F is the electric field. All derivations made in this chapter are for electron-only devices and the derivations for a

hole-only device are completely analogous.

A description of the electric field that arises from the presence of space-charge in the device is required to solve the drift-diffusion equation for electrons. SCLC is generally assumed to be one-dimensional, so the Poisson equation in one-dimension is given by:

$$\frac{dF(x)}{dx} = -\frac{qn(x)}{\varepsilon_r\varepsilon_0}. \quad (2.29)$$

In the derivation of the MG law, the diffusion current can be ignored (derived and explained in detail by Röhr *et al.*^{6,7}) and is given by:

$$J = qn\mu_n F, \quad (2.30)$$

Combining equation 2.29 and 2.30 gives:

$$Jdx = -\mu_n\varepsilon_r\varepsilon_0 F(x)dF(x). \quad (2.31)$$

This equation can be integrated over the spatial position, x , and the electric field F . Since the space-charge density extends across the entire thickness of the device, the boundary conditions for the spatial position are from 0 to x . In the limit of drift currents only, the electric field at the boundary, where $x=0$, equals zero ($F(0)=0$). Integration thus gives:

$$J \int_0^x dx' = - \int_0^F \mu_n\varepsilon_r\varepsilon_0 F(x)dF(x). \quad (2.32)$$

From this, the equation for the electric field distribution is given by:

$$F = -\sqrt{\frac{2Jx}{\mu_n\varepsilon_r\varepsilon_0}}. \quad (2.33)$$

Integration of the electric field over the thickness of the semiconductor gives an expression for the current density as a function of voltage:

$$V = \int_0^L F dx = - \left(\frac{8J}{9\mu_n \varepsilon_r \varepsilon_0} \right)^{\frac{1}{2}} L^{\frac{3}{2}}, \quad (2.34)$$

which, upon rearrangement, then yields the MG law (equation 2.26).

2.1.3.1.4 Equations with Traps (Non-Ideal Transport) As mentioned in section 2.1.1.7, real materials and devices have a degree of energetic disorder or chemical defects which leads to the trapping of charges. This can significantly alter the the actual shape and magnitude of the JV curves because the overall current is reduced when the number of charges free for conduction reduces.²⁶ Figure 2.6b shows the theoretically predicted JV trace for a semiconductor with a distribution of traps which are initially empty and neutrally charged when empty. The change in shape of the JV curve in this regime allows for the probing of trap states.

In conventional semiconductor physics, the onset voltage, V_{ons} , has been widely used to calculate the defect density, n_t , using:¹⁰

$$V_{\text{ons}} \approx \frac{qn_t L^2}{2\varepsilon_r \varepsilon_0} \quad (2.35)$$

With increasing voltage beyond V_{ons} , the current density increases sharply (3. $J \propto V^n$, $n > 2$, figure 2.6b) In literature, it is mostly reported as trap-filled-limited voltage, V_{tfl} , wrongly implying that this is the voltage at which all traps are filled. We will elaborate more on this in the next section.

2.1.3.1.5 Derivation of the Onset Voltage In one dimension, the trap density distribution function as a function of energy level E below the edge of the conduction band and a distance x from the contact for carrier injection can be written as:

$$h(E, x) = N_t(E)S(x), \quad (2.36)$$

where n_t and $S(x)$ represent the energy and spatial distribution function of traps, respectively. If the traps capture electrons only, the electric field $F(x)$ inside the specimen follows the Poisson equation:

$$\frac{dF(x)}{dx} = \frac{q[n(x) + n_t(x)]}{\epsilon_r \epsilon_0}, \quad (2.37)$$

where q is the electronic charge, ϵ is the static dielectric constant of the medium, $n(x)$ is the density of the injected free electrons and $n_t(x)$ the density of trapped electrons. The current density can be written as:

$$J = q\mu_n n(x)F(x), \quad (2.38)$$

where μ_n is the electron mobility, and $n_t(x)$ and $n(x)$ are given by:

$$n_t(x) = \int_{E_l}^{E_u} h(E, x)f(E)dE, \quad (2.39)$$

and

$$n(x) = N_C \exp(-E_{Fn}/k_B T), \quad (2.40)$$

where E_l and E_u are the lower and upper bounds of the trap levels, respectively, $f(E)$ is the Fermi-Dirac distribution function, N_C is the effective density of states in the conduction band, E_{Fn} is the quasi-Fermi level for electron traps, k_B is the Boltzmann constant and T is the temperature.

In the case of a trap free solid (ideal case), $n_t(x)=0$. If we multiply both sides of equation 2.37 with $2F(x)$ and substituting equation 2.38 for $n(x)$ into equation 2.37, we obtain:

$$2F(X)\frac{dF(x)}{dx} = \frac{d[F(x)]^2}{dx} = \frac{2J}{\varepsilon_r\varepsilon_0\mu_n}. \quad (2.41)$$

Integration of equation 2.41 and use of the boundary condition,

$$V \int_0^L F(x)dx, \quad (2.42)$$

where V is the applied voltage and L is the device thickness, yields the Mott-Gurney equation (equation 2.26).

As mentioned above, at low voltages, the JV characteristics follow Ohm's law, with the drift current density described by equation 2.38. When the density of injected carriers surpasses the background carrier density (n_0) we will observe a transition towards the space-charge limited regime, and this transition will occur when,

$$\frac{9}{8}\varepsilon_r\varepsilon_0\mu_n\frac{V^2}{L^3} \geq qn_0\mu_n\frac{V}{L}, \quad (2.43)$$

where the right hand term is drift current density due to the background carriers. Rearranging for V gives,

$$V_{\text{ons}} = \frac{8}{9} \frac{qn_0L^2}{\varepsilon_r\varepsilon_0}, \quad (2.44)$$

which is the onset voltage of the space-charge limited current regime, in the absence of traps. Note that n_0 is not necessarily the intrinsic charge but can also be related to the amount of traps or dopants in the film.⁷ It can also vary depending of the injection barrier at the contact and device thickness. Hence, it is difficult to make a relevant statement on n_0 values. In the presence of traps, for equation 2.35 to be valid, the assumption is made that the system has traps which are confined in single or multiple discrete energy levels. In this case, equation 2.36 becomes:

$$h(E, x) = H_a\delta(E - E_t)S(x), \quad (2.45)$$

2.1. Semiconductors

where H_a is the density of traps, E_t is the trap energy level below the edge of the conduction band, and $\delta(E-E_t)$ is the Dirac delta function. From equation 2.39 and 2.41, we obtain:

$$n_t(x) = \int_{E_l}^{E_u} \frac{H_a \delta(E - E_t) S(x) dE}{1 + g_n \exp[(E - E_{Fn})/k_B T]} \cong \frac{H_a S(x)}{1 + [H_a \theta_a / n(x)]}, \quad (2.46)$$

in which

$$\theta_a = \frac{g_n N_c}{H_a} \exp(-E_t / k_B T), \quad (2.47)$$

where g_n is the degeneracy factor (statistical weight) for the trap. θ_a describes the ratio of free carrier density to total (free and trapped) carrier density. Substitution of equation 2.46 into equation 2.37 gives:

$$\frac{dF(x)}{dx} = \frac{q}{\varepsilon_r \varepsilon_0} \left\{ n(x) + \frac{H_a S(x)}{1 + [H_a \theta_a / n(x)]} \right\}. \quad (2.48)$$

As mentioned earlier, for simplicity, it is assumed that the energy of the trap, E_t , is a shallow trap level located above E_{Fn} , and that the trap density is larger than the density of background carriers. Based on this, and by multiplying equation 2.48 with $2F(x)$ and substituting $n(x)$ from equation 2.38 into it, we obtain:

$$2F(x) \frac{dF(x)}{dx} = \frac{d[F(x)]^2}{dx} = \frac{2J}{\varepsilon_r \varepsilon_0 \mu_n \theta_a} [\theta_a + S(x)]. \quad (2.49)$$

Integration of equation 2.49 over the total thickness of the crystal or film, yields

$$J_{SCLC} = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_n \theta_a \frac{V^2}{L^3} \quad (2.50)$$

in which V is the applied voltage. As before with equation 2.44, the departure from the Ohmic regime occurs when the density of injected free carriers surpasses the

background density of carriers, but here its considered that only a certain fraction (θ_a) of the injected carriers is free. Therefore, the corresponding voltage onset point will be when,

$$\frac{9}{8} \epsilon_r \epsilon_0 \mu_n \theta_a \frac{V^2}{L^3} \geq q n_0 \mu_n \frac{V}{L}, \quad (2.51)$$

thus

$$V_{\text{ons}} = \frac{8}{9} \frac{q n_0 L^2}{\epsilon_r \epsilon_0 \theta_a}. \quad (2.52)$$

If this onset occurs when the free carrier density $n(x)=n_0$ then this voltage is extracted by substituting n_0 for $n(x)$ and substituting θ_a for $(n(x)/(n(x)+n_t))$. Under the assumption that the trap density is larger than the number of background carriers, equation 2.52 can be approximated to:

$$V_{\text{ons}} = \frac{q n_t L^2}{2 \epsilon_r \epsilon_0}. \quad (2.53)$$

Importantly, n_t is the number density of trapped carriers, and is distinct from H_a , which is to total number density of traps. The only condition under which they are equal is at zero Kelvin for a system with a single trap energy level. Additionally, here the term onset voltage (V_{ons}) instead of trap-filled-limited voltage (the voltage at which the traps are filled, V_{tfl}) is chosen purposely as equation 2.35 is derived under the assumption that the trap density is larger than the free charge density. In fact, the trap filling regime appears only if $n_t > n_0$ at a low voltage. Hence, the minimum trap density leading to a sharp inflection is given by the charge density n_{diff} at low voltages (where the current is dominated by diffusion) in the absence of traps and dopants.^{7,27,28} The minimum density of traps that is noticeable is given by:

$$n_{t,\text{min}} = n_{\text{diff}} = 4\pi^2 \frac{k_B T}{q^2} \frac{\epsilon_r \epsilon_0}{L^2}. \quad (2.54)$$

This can be derived under the assumption that the low voltage regime is not governed by Ohmic conduction of intrinsic carriers only, but rather by Ohmic conduction by a combination of the equilibrium carrier density, n , arising due to injection of carriers from the contact during Fermi level equilibration, and the intrinsic carrier density, n_i .

Whereas the current at low voltage is mostly due to the equilibrium concentration, the carrier density is not uniform, and the current is for that reason, not truly Ohmic. The charge-carrier density as a function of the spatial position inside the semiconductor in the electron-only device, $n(x)$, can to a good approximation be described analytically by,^{7,29}

$$n(x) = \frac{2\pi^2\epsilon_r\epsilon_0k_BT}{q^2L^2} \frac{1}{\cos^2[\pi(\frac{x}{L} - \frac{1}{2})]}. \quad (2.55)$$

The charge carrier density in the middle of the device, $n_0 = n(L/2)$, can be estimated using equation 2.55, and is given by:

$$n_0 = \frac{2\pi^2\epsilon_r\epsilon_0k_BT}{q^2L^2}. \quad (2.56)$$

The Ohmic conduction is not only due to charge carriers in the middle of the device, but due to all carriers in the semiconducting material. Therefore it is important to consider the entire thickness of the device, and thus the average charge-carrier density.⁷

The arithmetic mean of equation 2.55, $\langle n \rangle = L^{-1} \int_0^L n dx$, can not be calculated as the integral does not converge. However, it is possible to integrate n^{-1} , and the harmonic mean of the carrier density can be written as:⁷

$$\langle n \rangle_{\text{diff}} = \frac{1}{\frac{1}{L} \int_0^L n^{-1} dx}. \quad (2.57)$$

The integration yields:

$$\langle n \rangle_{\text{diff}} = 4\pi^2 \frac{k_BT}{q^2} \frac{\epsilon_r\epsilon_0}{L^2}. \quad (2.58)$$

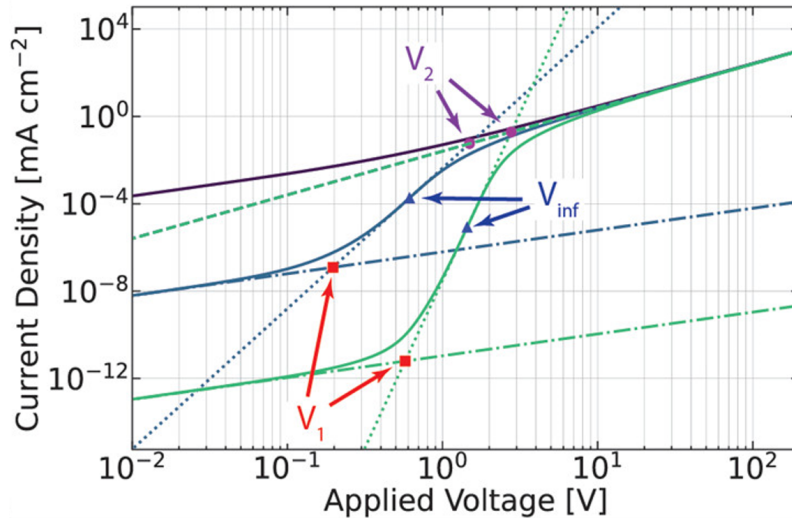


Figure 2.7: Simulated JV curves of an electron-only device with a 100 μm thick perovskite between two perfect electrodes with various trap densities. The green line represents the case with the largest trap density and the purple line the case with the smallest trap density. The dashed lines correspond to the different tangents with slopes of 1, 2, and >2 , and the red, blue, and magenta points correspond to construction of V_1 , V_{inf} , and V_2 , respectively. This simulation was performed by collaborator Dr. V.M. Le Corre.²⁷

This is equal to twice the carrier density in the middle of the device, $2n_0$.

For high-quality thin films, this means that a very thick film is required to be able to observe the trap-filling regime. The point that should be chosen as the voltage at which the traps are actually filled remains yet unclear. Different points that are chosen in the literature are shown in figure 2.7.²⁷ Most literature reports the voltage of the crossing point between the low-voltage tangent with a slope of 1 and the trap-filled-limited regime tangent with slope > 2 (V_1). Others use the crossing point between the tangent space-charge limited regime at high voltages and the trap-filled-limited regime V_2 . Lastly, some choose the middle of the trap-filled-limited regime V_{inf} .

With the work presented in this thesis (mainly chapter 4 and 5), in collaboration with numerical modelling from Dr. V.M. Le Corre *et al.*, it was assessed which voltage yields the most accurate estimate of the trap density.^{27,30,31} V_1 gives the worst estimate of trap density, and the error is largest when the density of traps is low and the transition between the two regimes is shallow. V_2 gives the most accurate value.

This is not so surprising as the Mott-Gurney regime is entered when all trap are filled, and the free carrier density becomes larger than the number of traps. Because of those discrepancies, this work uses V_{ons} as a figure of merit and more details on this will be presented in chapter 4 and 5.

2.1.3.1.6 Typical pitfalls of SCLC analysis As mentioned above, the carrier density and mobility could in principle be extracted from fitting Ohm's law in the regime where $J = V$ and the MG law to the JV curve in the regime where $J = V^2$, respectively, under the assumption that the semiconductor is intrinsic, and enough voltage has been applied such that the current is dominated by drift. The potential ease of equation 2.26 thus suggests why SCLC measurements are very widely used for the investigation of charge carrier transport in semiconductors.

However several pitfalls of SCLC measurements have arisen just from the simple characterisation of the different JV regimes, and are reported on in literature.²⁷ The most common ones are: (i) The use of non-ohmic or asymmetric contacts can lead to regimes with $m > 2$. Blakesley¹¹ and Röhr³² present methods to account for such contacts. Generally for such measurements, a built-in voltage should be avoided and the presence can be checked by performing a JV scan in both directions.³³ (ii) Factors such as intrinsic trap or dopant densities and diffusion can alter the interpretation of the low voltage regime.^{7,10,28,34} (iii) Depending on the thickness of the material and the size of the injection barriers, a linear JV regime can occur at high voltages and meaningful analysis of the MG law becomes beyond range.^{25,35} (iv) The way in which the trap filling regime should be modelled can vary.^{10,36–38}

In addition to these issues, perovskite bring new challenges to the electrical characterisation due to the mixed electronic-ionic nature of the materials, which will be discussed in the next sections. The challenges of using SCLC measurement for mixed

electronic-ionic systems will be discussed in chapter 4 and 5 and new methodologies will be provided.

2.2 Perovskites

2.2.1 Crystal Structure and Fundamental Properties

Perovskite is the nomenclature for the class of materials that adopt the same crystal structure as calcium titanate (CaTiO_3). This perovskite crystal structure with generic formula ABX_3 , where X is the anion (typically oxygen, halogens or alkali metals) and A and B are cations of different sizes (A being the larger organic part of the compound), is depicted in figure 2.8.

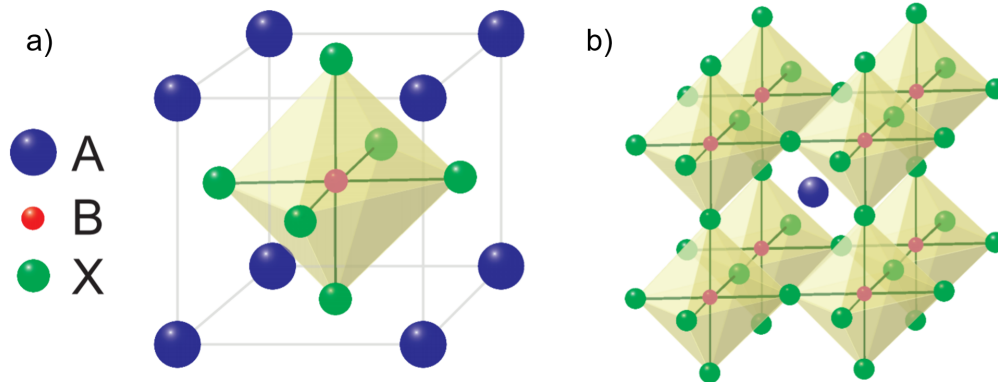


Figure 2.8: The perovskite crystal structure; a) the unit cell for a cubic ABX_3 perovskite lattice, where A and B are cations of different sizes, and X is an anion. The B site cation is surrounded by an octahedron of X anions; b) The octahedra form a cage around the A site cation when a greater number of unit cells are assembled together in the perovskite bulk.

A tolerance factor (t) has been introduced to determine if a stable three-dimensional ABX_3 structure can be formed from a combination of anions and cations. t is dependent on the ionic radii ($r_{A,B,X}$) of the A, B and X components via:

$$t = \frac{r_A + r_X}{(R_X + R_B)\sqrt{2}}. \quad (2.59)$$

A perfect cubic lattice structure has a tolerance factor equal to 1. However, typical perovskite structures have a tolerance factor between 0.8 and 1. For values of t below 0.8, formations of the lower symmetry lattices with tetragonal, rhombohedral, hexagonal and trigonal structures are favoured. If the tolerance factor is greater than 1, two-dimensional sheets of BX_6 , separated by large A-site cations, are formed. At the moment, most perovskites are used for photovoltaic purposes and within the broad range of possible perovskite components, the typical cations for the A-site include the organic small molecules methylammonium (MA^+) and formamidinium (FA^+) and the inorganic caesium (Cs^+). Although the B-site can be occupied by any divalent metal cation, lead (Pb^{2+}), tin (Sn^{2+}) and germanium (Ge^{2+}) seem to have the most appropriate properties for photovoltaic applications. The most common X-site halides are iodide (I^-), bromide (Br^-) and chloride (Cl^-). Due to the tunability of the chemical composition there is a plethora of advantageous material properties, including high absorption coefficients, band gap tunability and long carrier diffusion lengths for optoelectronic applications, but also superconductivity, thermoelectricity and anti-ferromagnetism.

2.2.2 The Rapid Evolution of Perovskites

Metal halide perovskites have been synthesised since as far back as 1882,³⁹ but it was not until the early 90's that their fundamental semiconducting and optoelectronic properties were first studied in the search for solution processable semiconductors.⁴⁰ The first works on successful metal halide perovskite solar cells were reported between 2006 and 2009, through the efforts to replace the dye sensitised solar cells by a perovskite as light absorbing layer.^{41,42} The real breakthrough came in 2012, when the liquid electrolyte was replaced by a solid-state hole conductor when Lee *et al.*⁴³ and Kim *et al.*⁴⁴, almost simultaneously, developed stable perovskite solar cells with power conversion efficiencies around 10%. The remarkable publication by Lee *et al.* reported that an insulating mesoporous Al_2O_3 scaffold leads to equally well performing

devices as by using the well-known mesoporous TiO_2 , which was essential for electron extraction in dye sensitized solar cells.⁴³ This study suggested for the first time that metal halide perovskites are, besides being simple absorber materials, also capable of long range electron transport similar to inorganic semiconductors. In 2013, Ball *et al.* showed that $\text{MAPbI}_{3-x}\text{Cl}_x$ can be implemented into a planar heterojunction format, highlighting that the perovskite absorber is capable of transporting both electrons and holes to the respective n- and p-type contacts.⁴⁵ This planar heterojunction device architecture allows for easy solution processing deposition and various vapour deposition techniques, and presents a promising route to commercialisation.

2.2.3 Stability

Photovoltaic devices have to undergo standard stability tests sets done by the International Electrotechnical Commission (IEC) in order to be commercialised. These tests require the solar cell to sustain 200 thermal cycles between $-40\text{ }^\circ\text{C}$ and $+85\text{ }^\circ\text{C}$ with a maximum deviation of the photocurrent of $\pm 2\%$, measured at peak power above $25\text{ }^\circ\text{C}$.⁴⁶ Perovskites-based devices have to sustain sufficient chemical and structural stability towards the environment, while maintaining its good optoelectronic properties. Chemical stability refers to the materials capability to be resistant to reactive species such as humidity and oxygen, and structural stability refers to the ability of a material to stay in a single crystalline phase across a wide range of temperatures. Heating or cooling perovskites can induce a phase transition. Such transitions can cause distortions in the crystal lattice and can impact the material properties. MAPbX_3 has been reported to remain crystallographically stable over a wide range of temperatures.^{43,44,47}

However, FAPbI_3 , which allows for the highest theoretical efficiency, is meta stable under ambient conditions, and transitions into the non-perovskite phase, which has an undesirable wider band gap.^{47,48} Major efforts are directed at finding approaches to suppress phase change, but the inherent vulnerability to moisture possesses a a major

challenge as the phase stability of perovskites is of paramount importance for their practical use. Chapter 6 will discuss a possible route for the phase stabilisation of FAPbI_3 while maintaining its excellent intrinsic properties.

2.2.4 Mobile Ions

As opposed to conventional semiconducting devices for photovoltaics, halide perovskites are mixed ionic-electronic semiconductors. Charged mobile ions (and their vacancies) inside these halide materials can screen the bulk material from externally applied bias, which can limit the performance of perovskites in applications.⁴⁹ Ion migration in a material refers to the hopping displacement of ionic species between interstitials or vacancy sites.⁵⁰ The concentration of mobile ions is controlled by point defects, where Frenkel defects (interstitial and vacancy created from the same ion) and Schottky defects (anion and cation vacancy occurring together), formed in stoichiometric units to maintain the overall neutral charge, are the most common processes.^{51–54}

A schematic of the different types of defects is depicted in figure 2.9. The defect formation energy is predicted to be low, as the enthalpic cost of defect formation is offset by the gain in entropy of the system.⁵⁵ This implies a thermodynamic driving force for the formation of a high concentration of vacant lattice sites which is independent of the growth conditions.⁵²

Externally applied forces such as voltage can cause ion distribution across the perovskite and ion accumulation at the electrodes, equivalent to p- and n-type doping. The process of ion migration in perovskites has received broad attention as it possibly is the origin or important contributing factor of processes such as giant switchable photovoltaic effects, diminished transistor behaviour at room temperature,⁵⁶ giant dielectric constant in the low frequency range,⁵⁷ light-induced phase separation,⁵⁸ and,

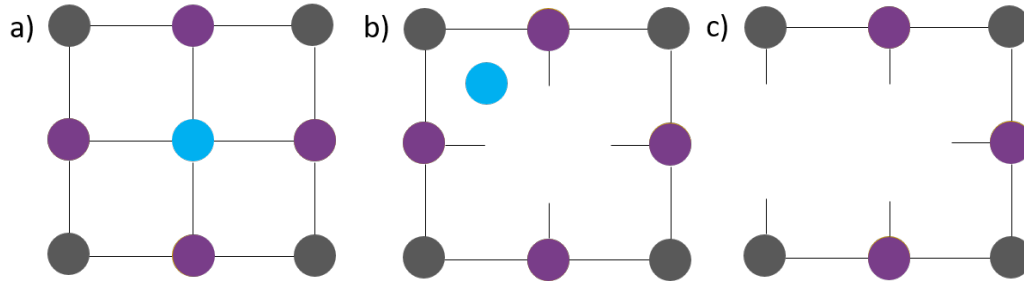


Figure 2.9: Defects in the perovskite crystal lattice (blue, grey and purple dots represent the (A-, B-, and X-site ions, respectively); a) perfect lattice; b) Frenkel defect; c) Schottky defect.

importantly, hysteresis in the JV curves.^{49,59} Typically, the halide anions are identified as being majorly responsible for ionic motion due to their higher diffusion coefficient, lower activation energy and higher density compared to other ionic species.^{60–62} Recently, it has been reported that the A-site cations such as Cs^+ , MA^+ , FA^+ and even H^+ should be considered as possible migrating species too. Generally, the ionic motion depends largely on the system that is studied and needs to be accounted for.

2.2.5 Hysteresis

Perovskite-based devices show substantial mismatch between the JV curves measured from short circuit to open circuit and *vice versa*. The hysteresis in the JV curves in perovskites is much slower, more complex and anomalous, compared to conventional silicon solar cells, and can lead to erroneous estimation of device performances.⁵⁵ Numerous theories have been proposed to elucidate the underlying causes, like ferroelectric polarisation,⁶³ ion migration,⁵⁹ deep trap states and carrier dynamics at different interfaces,⁶⁴ and the origin is a highly debated topic. Furthermore, hysteresis is reported to dependent on measurement conditions such as voltage scan rate and direction, pre-biasing conditions, illumination conditions and history of applied bias, as well as device architecture and contact material. Hysteresis occurs on timescales corresponding to the migration of ions,^{53,59,65–68} and Snaith and co-workers showed numerically that hysteretic effects in perovskites originate from a combination of

electron trapping and ionic transport throughout the perovskite.⁴⁹

Over the years, the dramatic impact of ionic species on the JV characteristics has been widely reported on. Surprisingly, the effect on the JV curves extracted from SCLC measurements has been mostly ignored, and there are very few reports highlighting the difference between forward and reverse JV traces. Therefore chapter 4 discusses this extensively and introduces a new measurement methodology to circumvent hysteresis and allow for correct extraction of intrinsic properties of the perovskite.

2.2.6 Single Crystal Perovskites

The crucial issues discussed above must be tackled before the industrial-scale use of perovskites is possible. Whereas an ever-growing number of studies focus on improving optoelectronic properties of perovskite-based devices to increase device efficiency, there is an urgent need for a detailed understanding of perovskites at a more basic level. Therefore, this work focuses on macroscopic single crystal (SC) perovskites. SCs provide an ideal platform for studying the fundamental properties of optoelectronic materials due to the absence of grain boundaries, high crystallinity in the bulk and reduced trap density.

Chapter 4 and 5 focus on decoupling ionic and electronic motion to understand the intrinsic charge carrier transport properties of single crystals, and particularly the effect of ionic species in single crystals on the JV characteristics during SCLC measurements. In chapter 6, single crystals are used to study the suppression of phase instability upon the addition of additives. Single crystals grant an excellent way to distinguish between the effect on the bulk and the surface. Whether it is for the understanding of charge transport or the effect of additives, the improved understanding is translatable to perovskite thin film devices, and it can help to push development of the optoelectronic

properties as well as the stability and crystallinity of thin films.

Moreover, in many regards, single crystals outperform polycrystalline films. Their superior optoelectronic properties demonstrate potential applications such as photovoltaic devices, light-emitting diodes, lasers, x-ray- and photo- detectors.

2.3 Computational Modelling

For a detailed understanding of the underlying device physics on electronic and ionic behaviour within perovskite single crystals, a device model describing the operation of perovskite solar cells and quantitatively explaining the role of contacts, recombination, and drift and diffusion of charge carriers and ions is used for the research in Chapter 4 and Chapter 5. Those chapters combine experimental research with computational modelling to understand and validate the underlying physics of perovskite-based devices. The computational work in these chapters has been performed in collaboration with Dr. V.M. Le Corre and Prof. Dr. L.J.A. Koster from the University of Groningen.

2.3.1 Physics of the Device Model

For this study, a one-dimensional device model developed by Prof. Dr. L.J.A. Koster and co-workers at the University of Groningen is used.⁶⁹ It is based on drift and diffusion of charge carriers through the device and on the effect of space-charge on the electric field by self-consistently solving the continuity equations and Poisson's equation.^{27,69–72} All JV curves in this work are simulated under dark conditions, and the active material includes both mobile ions and electron traps.

The current continuity equations are:⁷³

$$\frac{\partial}{\partial x} J_n(x) = qU(x), \quad (2.60)$$

$$\frac{\partial}{\partial x} J_p(x) = -qU(x), \quad (2.61)$$

where $U(x)$ is the net generation rate, i.e., the difference between generation and recombination of free carriers.

The transport of charge carriers is governed by diffusion and electrically induced drift, and the electron and hole currents can be written following equation 2.27 and 2.28, respectively. For convenience, they are given here again for electrons:⁷³

$$J_n(x) = qD_n \frac{\partial n(x)}{\partial x} - qn(x)\mu_n \frac{\partial V(x)}{\partial x}, \quad (2.62)$$

and for holes

$$J_p(x) = -qD_p \frac{\partial p(x)}{\partial x} - qp(x)\mu_p \frac{\partial V(x)}{\partial x}, \quad (2.63)$$

where q is the electric charge, $V(x)$ is the potential, $n(x)$ and $p(x)$ are electron and hole concentrations, μ_n and μ_p are electron and hole mobilities, D_n and D_p are electron and hole diffusion constants, which obey the Einstein relation.⁷³

The device model is one-dimensional, and the position within the device is given by x . The left contact is set at $x = 0$ and the right contact at $x = L$, in which L is the thickness of the device. The electrostatic potential throughout the device is solved from Poisson's equation:

$$\frac{\partial^2}{\partial x^2} V(x) = -\frac{q}{\epsilon_0 \epsilon_r(x)} (n(x) - p(x) + C_i(x)). \quad (2.64)$$

C_i can represent other types of charge in the system such as: (1) X_c and X_a as the cationic and anionic defect densities, respectively; (2) $N_A^-(x)$ and $N_D^+(x)$ as the

2.3. Computational Modelling

ionised p-type and n-type doping in the hole transporting layer and electron transporting layer, respectively; (3) Q_t^- and Q_t^+ as the charged electron and hole traps, respectively.

The Poisson equation can be rewritten as:

$$\frac{\partial^2}{\partial x^2} V(x) = -\frac{q}{\epsilon_0 \epsilon_r(x)} (n(x) - p(x) + X_a(x) - X_c(x) + N_A^-(x) - N_D^+(x) + Q_t^- - Q_t^+). \quad (2.65)$$

In the case of immobile ions, the ions are distributed with a uniform density across the material, and if the ions are mobile, the drift-diffusion equation is solved under the assumption that the ionic current is zero. The ion density and the derivative of it is only dependent on the electric field, which is solved iteratively, and the electric field can be calculated from a first guess for the distribution of electrons, holes and traps. If the ion density is known, the ionic distribution can be calculated and by solving the Poisson equation the the number of electrons, holes and ions can be extracted.

The sign of the trap when filled is $Q_t \in \{-1, 0, +1\}$, and the occupation probability of the trap is $f_{t, v=n,p}$:

$$f_{t, v=n,p} = \left[1 + \left(\frac{g_{0,v}}{g_{1,v}} \right) \left(\frac{v}{N_{CV}} \exp \left(\frac{E_{\text{trap}}}{V_t} \right) \right)^\alpha \right]^{-1}, \quad (2.66)$$

where $g_{0,1}$ are the degeneracy factors of empty and filled trap levels, respectively, N_{CV} is the effective density of states (DOS) of the conduction and valence band, $E_{\text{trap}} (= E_g/2)$ is the trap energy level in the middle of the band gap, α is the sign of the trapped carrier (-1 for electrons and +1 for holes), and V_t is the thermal voltage ($V_t \sim 25$ meV at room temperature). $g_0/g_1 = 1$ as the degeneracy of the traps is neglected here.

2.3. Computational Modelling

To numerically solve the equations above, the boundary condition on the electrostatic potential is given by:

$$q(V(L) - V(0) + V_{\text{app}}) = W_{\text{c}} - W_{\text{a}}, \quad (2.67)$$

where V_{app} is the applied bias and $\chi_{\text{m,a}}$ and $\chi_{\text{m,c}}$ are work functions of the anode and cathode, respectively. The built-in potential is then given by $V_{\text{bi}} = (\chi_{\text{m,c}} - \chi_{\text{m,a}}/q)$.

Boltzmann statistics describe the boundary conditions for electrons at the anode ($x=0$) by:⁷³

$$n(0) = N_{\text{c}} \exp\left(-\frac{E_{\text{g}} - \phi_{\text{p}}}{k_{\text{B}}T}\right), \quad (2.68)$$

and for holes at the anode:

$$p(0) = N_{\text{v}} \exp\left(-\frac{\phi_{\text{p}}}{k_{\text{B}}T}\right), \quad (2.69)$$

where N_{c} is the effective DOS of both the conduction and valence band and ϕ_{p} is the injection barrier height (in eV) for holes. For the cathode ($x = L$) holds:

$$n(L) = N_{\text{c}} \exp\left(-\frac{\phi_{\text{n}}}{k_{\text{B}}T}\right), \quad (2.70)$$

$$p(L) = N_{\text{v}} \exp\left(-\frac{E_{\text{gap}} - \phi_{\text{n}}}{k_{\text{B}}T}\right), \quad (2.71)$$

where ϕ_{n} is the injection barrier height (in eV) for electrons.

If n_{i} is assumed to be the intrinsic carrier concentration and E_{trap} is the trap energy in eV then:

$$n_{\text{i}} = N_{\text{c}} \exp\left(-\frac{E_{\text{c}} - E_{\text{trap}}}{k_{\text{B}}T}\right), \quad (2.72)$$

$$p_i = N_V \exp\left(-\frac{E_{\text{trap}} - E_V}{k_B T}\right). \quad (2.73)$$

The model uses Gummel iteration to solve the continuity equations and Poisson's equation. The flow diagram of the simulation model is given in the appendix in appendix A in figure (A.1).

As a first step, a guess is made for the potential and the carrier densities, then the Poisson equation is solved and a correction δV to the potential is calculated and then subsequently added to the guessed potential. The continuity equations are solved for the carrier densities using the new potential as input value. This process is iterated until convergence is reached. Further detailed of the process are in reference⁷⁴.

2.3.2 Modelling Predictions on Current-Density Voltage Characteristics

In inorganic semiconductors it is usually assumed that traps are neutral when empty and negatively charged when filled with electrons. A negatively charged trap when filled can act as a potential barrier for electrons, which impedes the electron transport and affects long-range mobility. In perovskites, cations, or the vacancies of anions can induce trap states. In this case, traps are positively charged when empty and neutral when filled with electrons.⁷¹ The device model shows that in this case all traps are filled directly when performing the JV scan, and the electron transport is relatively unaffected by the traps. This is elaborated more on in section 5.2 in chapter 6.

In the simulations in this work where ions are included, initially a homogeneous density of ions (number of anions = number of cations) is set and the ion distribution is stabilised at 0 V. The subsequent JV sweep is sufficiently fast that ions do not redistribute during the sweep.

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Device Fabrication and Experimental Methods

This chapter describes the materials, device fabrication steps, and characterisation methods utilised in this thesis.

3.1 Device Fabrication

3.1.1 Single Crystal Synthesis

The controllable synthesis of high-quality perovskite single crystals is of fundamental importance for their applications in the photovoltaic and photoelectric fields. There exist a number of growth strategies such as the solution temperature lowering method and anti-solvent vapour-assisted crystallisation method, but this work focuses on the fabrication of large high-quality single crystals from a solution using the inverse temperature crystallisation method.

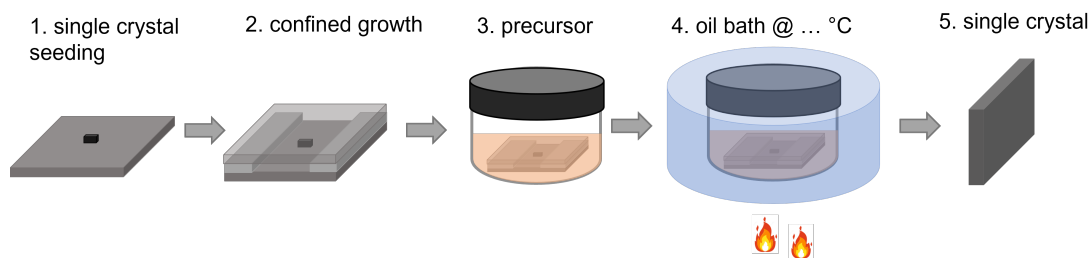


Figure 3.1: Schematic illustration of the device fabrication process: 1) single crystal seeding; 2) confined growth to control the crystal size; 3) precursor solution added; 4) crystal growth in oil bath at elevated temperature; 5) single crystal taken out of solution.

3.1.1.1 Inverse Temperature Crystallisation Method

In the process of the inverse temperature crystallisation method, the precursor solution is heated at a fixed temperature to grow single crystals.¹ During the growth process, at the beginning, the surface of the solution is in a saturated state because of the volatilisation of the solvent, while the bottom of the solution is unsaturated. As the solvent decreases, the concentration will exceed the solubility of precursors because of the convection inside the bottle, which leads to the growth of single crystals.² A pre-synthesized seed can be used as a nucleation site for the growth of larger crystals.

A schematic of the single crystal growth process is depicted in figure 3.1. To control the thickness down to the micrometre scale, a small chamber was constructed using two thin glass plates of different thicknesses placed on the bottom of the glass vial with a gap in between and a cover glass on top, as depicted in figure 3.1 (2).

Chapter 4 focuses on methylammonium lead bromide (MAPbBr_3) single crystals, chapter 5 on MAPbBr_3 and methylammonium lead iodide (MAPbI_3) single crystals, and chapter 6 on formamidinium lead iodide (FAPbI_3) single crystals. The exact details of the fabrication processes of these single crystals will be discussed below.

3.1. Device Fabrication

Chemicals and reagents N,N-Dimethylformamide (DMF) (68-12-2), PbBr_2 (10031-22-8), $\text{CH}_3\text{NH}_3\text{Br}$ (6876-37-5), $\text{CH}_3\text{NH}_3\text{I}$ (14965-49-2), $(\text{CH}_2\text{NH}_3)_2\text{Cl}_2$ (57166-92-4), Hexamethylenetetramine (HMTA) (100-97-0), NH_4Cl (12125-02-9), γ -butyrolacton (GBL) (96-48-0), and d6-dimethyl sulfoxide (DMSO) (2206-27-1) were purchased from Sigma-Aldrich. PbI_2 (10101-63-0) was received from TCI. All salts and solvents were used as received and without any further purification.

MAPbBr₃ Single Crystals: PbBr_2 (3.67 g) and MABr (1.11 g) were dissolved in 10 mL of DMF. The solution was stirred until fully transparent. This solution was filtered with a 25 mm diameter 0.45 μm PVDF filter. A 4 mL sample of the filtrate was placed in a vial which contained a chamber with a seed MAPbBr₃ crystal. A chamber was used to control the size of the crystals. The vial was kept in an oil bath undisturbed at 80 °C for 5 h. A free-standing, millimetre sized crystal was taken out of the vial once formed and quickly rinsed by pure DMF solvent.

MAPbI₃ Single Crystals: PbI_2 (5.53 g) and MAI (1.91 g) were dissolved in 10 mL of GBL. The solution was stirred at 55 °C until fully transparent. This solution was filtered with a 25 mm diameter 0.45 μm GMF filter. A 4 mL sample of the filtrate was placed in a vial which contained a seed MAPbI₃ crystal. A chamber was used to control the size of the crystals. The vial was kept in an oil bath undisturbed at 100 °C for 12 h. A free-standing, millimetre sized crystal was taken out of the vial once formed and dried with clean room tissue.

FAPbI₃ Single Crystals: PbI_2 (4.61 g) and FAI (1.71 g) were dissolved in 10 mL of GBL. The solution was stirred at 60 °C for one hour. For the passivated crystals, a passivation agent was added to the solution. Then the solution is filtered with a 25 mm diameter 0.45 μm GMF filter. Both solutions were stirred at 60 °C overnight. This solution was filtered with a 25mm 0.45 μm GMF filter. A 4 mL sample of the filtrate was placed in a vial which contained a seed crystal. A chamber was used to

control the size of the crystal. The vial was kept in an oil bath undisturbed at 95 °C for 4 hours. The crystals were then dried in a vacuum oven at 180 °C. Free-standing, millimetre-sized crystals were taken out of the vial once formed.

3.1.1.2 Single Crystal Device Fabrication

To turn the crystals in to functional devices for electrical characterisation purposes, 120 nm gold electrodes were evaporated on both of the larger faces of the single crystal by an evaporator (Kurt J. Lesker, Nano36) at a 0.5 A s^{-1} deposition rate.

3.2 Characterisation

The methods used to characterise the single crystals are described here.

3.2.1 Electrical Characterisation

3.2.1.1 Space-Charge Limited Current Measurement

To measure the electron transport properties of perovskite single crystals in the space-charge limited current (SCLC) measurement, two gold wires were attached to either side of the free standing crystal and four-probe SCLC measurements were performed. The JV characteristics were measured using a computer-controlled 2400 Series Keithley source meter and the devices were under N_2 conditions in the dark. The vacuum pump (Leybold vacuum, PT 70 F-Compact) pumped the system down to 10^{-4} mbar.

Temperature-dependent measurements were performed done to extract electronic conductivity under low temperature conditions. The measurements were carried out in vacuum (10^{-6} mbar) in a nitrogen cryostat. The samples were brought in via the top-loading sample probe. The temperature was varied from room temperature down to 80 K and back to 330 K.

3.2.1.2 Transient Photoconductivity Measurement

Transient photoconductivity (TPC) measurements were done to extract the charge carrier mobility. An Nd:YAG laser (Ekspla NT342A) was tuned to be used at various wavelengths. The laser was pumped at 10 Hz with 3.74 ns pulses (full-width-half-maximum (FWHM)) and used at the range of fluences attenuated by an optical density to filter such that it allows for the generation of various carrier densities. The pulsed light from the laser illuminated the entire sample area uniformly to excite the material. A small DC bias ($< 5 \text{ mV mm}^{-1}$) was applied across the in-plane (lateral) electrodes. A fixed resistor was put in series with the sample in the circuit to be $< 1\%$ of the sample resistance. The voltage drop across the variable series resistor was monitored through a parallel oscilloscope with 1 MQ input impedance, to determine the potential drop across the two in-plane gold electrodes on the sample. More detail is reported in reference³. The TPC measurement was done together with collaborators J. Lim and M. Kober-Czerny.

3.2.1.3 Time-resolved Photoluminescence Measurement

For the time-resolved photoluminescence measurements (TRPL), the samples were mounted in air and photoexcited by a 398 nm picosecond pulsed diode laser (PicoHarp, LDH-D-C-405M). The resultant PL was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558), which directed the spectrally dispersed PL onto a photon-counting detector (PDM series from MPD), whose timing was controlled with a PicoHarp300 TCSPC event timer. Laser fluences of between 2 and 1500 nJ cm⁻² were used, with a laser repetition rate of 2.5 MHz. The PL decay traces were each fitted by a stretched exponential function $I = I_0 e^{-(t/\tau)^\beta}$, where β is the distribution coefficient and τ is the time taken for the PL intensity to drop to I_0/e . Such stretched exponential functions have been used to phenomenologically account for the presence of a local distribution of monoexponential decay rates, whose average

lifetime is given by $\tau_{av} = (\tau/\beta)\Gamma(1/\beta)$, where Γ is the gamma function.^{4,5} The TRPL measurement was performed by collaborator Dr. A.D. Wright.

3.2.1.4 Terahertz Mobility Measurement

The electrical mobility of the single crystals was measured using optical-pump-THz-probe spectroscopy (OPTPS) in reflection geometry. The single crystals were photoexcited by a 35 fs pulsed laser with central wavelength at 400 nm, which generates free charge carriers and results in an increase of the reflected THz signal. The electrical mobility was extracted using the method detailed in reference⁶. These measurements were performed by collaborator Dr. C. Xia.

3.2.2 Optical and Spectroscopic characterisation

3.2.2.1 Optical Microscopy Imaging

The optical microscope images were acquired in reflection and transmission mode with a LEICA M205C microscope. Polarization filters, dark field and bright field modes were applied for different visualisations of the crystal microstructure analysis.

3.2.2.2 Scanning Electron Microscopy

Top surface and cross-sectional imaging of single crystals were measured using a FEI Quanta 600 FEG environmental scanning electron microscope (SEM). Accelerating voltages between 4-15 kV were employed for various analysis.

3.2.2.3 Raman Spectroscopy

Raman spectra were acquired with a Jobin Yvon T64000 triple spectrometer and an Andor DU420A-OE CCD. The spectrometer was calibrated with the 520.7 cm^{-1} line of a Silicon wafer before each measurement. Samples were excited with a Ventus solo Nd:YAG laser ($\lambda = 532 \text{ nm}$) and the incident laser irradiation of the samples

was strictly kept at intensities below 5 W/cm^2 to prevent laser induced degradation. These measurements were performed by collaborator B. Sturdza.

3.2.3 Material characterisation

3.2.3.1 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance measurements were performed where a two-channel Bruker Avance III HD Nanobay 400 MHz instrument running TOPSPIN 3 equipped with a 5 mm z-gradient broadband/fluorine observation probe is used. The signal from residual non-deuterated DMSO solvent was used for reference. These measurements were performed by collaborators B. Gallant and S. Collavini.

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Space-Charge Limited Current Measurements on Metal Halide Perovskites

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Toward Understanding Space-Charge Limited Current Measurements on Metal Halide Perovskites, ACS Energy Letters, 5, 376-384, 2020. Copyright 2022 American Chemical Society.

4.1 Context and Summary

Metal halide perovskite semiconductors have sprung to the forefront of research into optoelectronic devices and materials, largely because of their remarkable photovoltaic efficiency records above 25% in single-junction devices and 28% in tandem solar cells, achieved within a decade of research. Despite this rapid progress, ionic conduction

within the semiconductor still puzzles the community and can have a significant impact on all metal halide perovskite-based optoelectronic devices because of its influence upon electronic and optoelectronic processes, as mentioned in chapter 3. This phenomenon thus also makes the interpretation of electrical characterisation techniques, which probe the fundamental properties of these materials, delicate and complex. For example, space-charge limited current measurements are widely used to probe defect densities and carrier mobilities in perovskites. However, the influence of mobile ions upon these measurements is significant. In this chapter, the effect of mobile ions upon electronic conductivity during space-charge limited current measurements of methylammonium lead tribromide (MAPbBr_3) single crystals is reported, and it is shown that conventional interpretations deliver erroneous results. Then, a pulsed-voltage space-charge limited current procedure is introduced to achieve reproducible current-voltage characteristics without hysteresis. From this revised pulsed current-voltage sweep, a lower bound trap density value of $2.8 \pm 1.8 \times 10^{12} \text{ cm}^{-3}$ in MAPbBr_3 single crystals is elucidated. This work represented here will help achieving more accurate characterisation of halide perovskite semiconductors and ultimately more effective device optimisation.

4.2 Introduction

The dawn of a new era in optoelectronic research has emerged with the recent studies on organic-inorganic metal halide perovskites.¹⁻³ Their long carrier lifetimes, sufficient charge carrier mobility, ensuing long-range charge transport,⁴ low levels of electronic disorder, and low cost device production render perovskites as one of the most exceptional and competitive optoelectronic materials for many applications such as photovoltaic devices,^{1,5} field-effect transistors,⁶ light-emitting diodes,⁷ photo and radiation detectors,⁸ and lasers.^{9,10} The accurate characterisation of a semiconductor's fundamental properties is important for the development of electronic and optoelectronic devices. Among the various charge transport characterisation techniques available,¹¹ the space-charge limited current (SCLC) measurement is one of the most

commonly used steady-state techniques. By measuring dark JV characteristics, the electron- and hole-transport and injection properties can be studied.^{12–15} More details on the principles and pitfalls of SCLC measurements are given in section 2.1.3.1 in chapter 2.

In principle, for unipolar conduction in a perfect semiconductor, the JV curve follows Ohm's law at low voltages (1. $J \propto V$ in figure 4.1a), and when the injected free carrier concentration exceeds the background carrier density, the current is limited by the build-up of space charge (2. $J \propto V^2$ in figure 4.1a) and follows the MG law (equation 2.26).¹⁶ As explained in section 2.66 in chapter 2, the presence of traps significantly changes the shape and magnitude of the JV characteristics.¹⁷ The predicted JV curve is depicted in figure 4.1b. The onset voltage V_{ons} is often used to calculate the defect density using equation 2.35.¹⁵ The derivation of onset voltage is given in chapter 2 in section 2.1.3.1.5, and the explicit assumptions under which n_t in equation 2.35 equals the total trap density in the semiconductor are discussed in chapter 2 in section 2.1.3.1.5. With increasing voltage beyond V_{ons} , the current density increases sharply (3. $J \propto V^n$, $n > 2$ in figure 4.1b), and when all traps are filled, the current follows the MG law in the absence of trapping (2. $J \propto V^2$ in figure 4.1b). As discussed in section 2.1.3.1.5 and 2.1.3.1.6 in chapter 2 the analysis of SCLC measurements is often oversimplified as the required assumptions are often not fully met and their consequences are overlooked.

Hybrid perovskites bring some new challenges of their own as they are distinct from most conventional semiconductors because they exhibit characteristics of both electronic and ionic conduction. The presence of these mobile ionic species has the potential to profoundly disturb device characteristics, because they may shield the bulk material from externally applied voltages and thus affect the total electronic current injection, transport and extraction. For instance, consensus has been reached that mobile ions play a major role in the origin of hysteresis in JV curves of solar cell

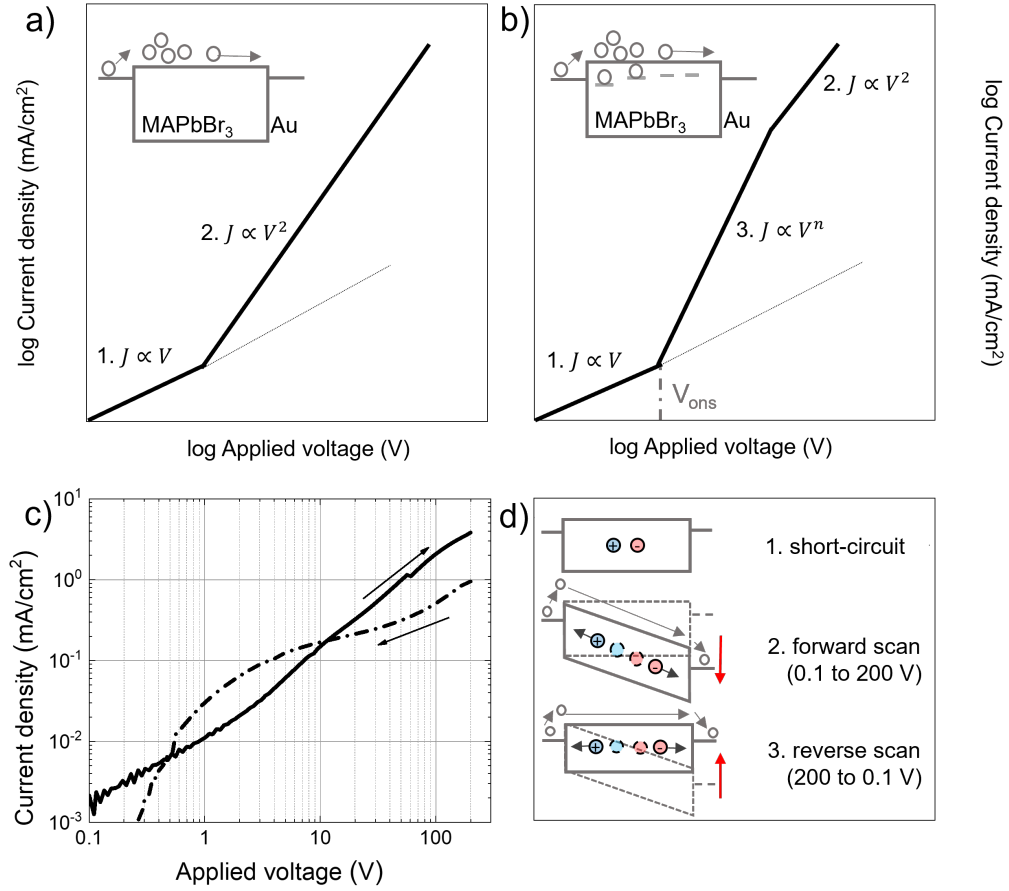


Figure 4.1: Schematic illustration of the principle and hysteresis in SCLC measurement in an electron-only device; a) SCLC behaviour for a trap-free semiconductor. Two charge transport regions are visible: 1. $J \propto V$ Ohmic region and 2. $J \propto V^2$ SCLC region; b) SCLC behaviour for a semiconductor with trap states. Three charge transport region are visible: 1. $J \propto V$ Ohmic region, 3. $J \propto V^n$, $n > 2$ trap-filled limited region, and 2. $J \propto V^2$ SCLC region in the absence of trapping. Panels a and b show example schematics of JV curves, and their scales are dependent on the sample characteristics and dimensions; c) Large hysteresis between forward (solid line) and reverse (dashed line) JV traces during the SCLC measurement; d) Schematic illustration of ion movement during the SCLC measurement. At short circuit (1) mobile ions are distributed across the crystal. Upon application of a positive voltage during the forward scan (2), mobile ions drift toward the electrode interfaces. Mobile ions are still displaced toward the electrode interfaces during the reverse scan (3).

devices.^{18–20}

Despite the research effort toward exploring the origins of this ubiquitous hysteresis in JV curves for solar cells, there is a large body of published literature on SCLC measurements of metal halide perovskite single crystals and thin films that does not report data for both forward (increasing voltage) and reverse (decreasing voltage)

directions in JV sweeps nor mentions the possible influences of mobile ions.^{21–43}

A redistribution of ionic charge due to a continuously applied electric field during the SCLC measurement, however, is in fact likely to influence the electronic charge carrier transport in perovskites and thus the shape of the JV curve. Therefore, characterising charge carrier properties without considering mobile ions is prone to misinterpretation and can lead to systematic errors that result in misunderstanding of the intrinsic electronic properties of perovskites. Because SCLC is such a popular and, in principle, simple measurement to perform, it is crucial to understand the effect of mobile ions under an applied electric field for an accurate characterisation of the electrical properties. This chapter will show that V_{ons} in MAPbBr₃ single crystals can differ by more than an order of magnitude when the scan is swept between forward (0.1 to 200 V) and reverse (200 to 0.1 V) directions. This hysteresis is explained by analysing the role of the applied electric field during the SCLC measurement on the mobile ions. To achieve reproducible JV curves without hysteresis, a pulsed voltage (PV)-SCLC method is introduced, which pseudolocalises nominally mobile ions during the JV sweep. This enables the measurement of the intrinsic electronic properties in perovskite semiconductors. Using the PV-SCLC method, the ionic conductivity is decoupled from electronic conductivity in macroscopic MAPbBr₃ single crystals during SCLC measurements, and a lower bound of the trap density in MAPbBr₃ single crystals of $2.8 \pm 1.8 \times 10^{12} \text{ cm}^{-3}$ is calculated.

4.3 Results and Discussion

4.3.1 Hysteresis in Current-Voltage Curves during Space-Charge Limited Current Measurements

For this study, freestanding, millimeter-sized macroscopic MAPbBr₃ single crystals are prepared with 120 nm thick gold electrodes on either side of the crystal for carrier

injection and extraction, as described in chapter 3. As shown in figure 4.1c, there is a significant difference between the JV scans performed in the forward (solid black line) and reverse (dashed black line) bias voltage directions during the SCLC measurement. Surprisingly, this is the first time hysteresis in SCLC measurements of perovskites has been acknowledged. Figure 4.1d shows the principles of the SCLC measurement, with the assumption that there are mobile ionic species (that could originate from vacancies or interstitials) in the perovskite crystal, to give a better understanding of the hysteretic behavior. Under short-circuit conditions, it is assumed that mobile ions are distributed across the crystal (1. short circuit in figure 4.1d). A positive voltage at the electron extraction contact during the forward voltage scan results in the drift of negatively charged mobile ions to the electron extraction electrode, while simultaneously positively charged mobile ions drift toward the opposite electrode (2. forward scan in figure 4.1d). While the scanning direction is changed from high voltages back to short circuit, the internal electric field of the system is still under positive voltage conditions, and consequently mobile ions are still displaced toward the electrode interfaces (3. reverse scan in figure 4.1d). This causes a “positive prebias effect” during the reverse voltage scan. It is postulated that the difference in the position of mobile ions, caused by the applied electric field during the JV sweep, explains the hysteresis in the JV traces. Additionally, it is assumed that the mobile ions require a certain diffusion time under short-circuit conditions to migrate back to their initial position after drifting to electrode interfaces because of the applied electric field during the voltage sweep.

4.3.2 Localising Mobile Ions

To assess the influence of drifting mobile ions on electronic current extraction, the localisation of mobile ionic species is controlled as a function of time, by varying the waiting time (termed as interval time, t_{int}) between subsequent voltage sweep cycles, where one voltage sweep cycle refers to both forward and reverse scan. The

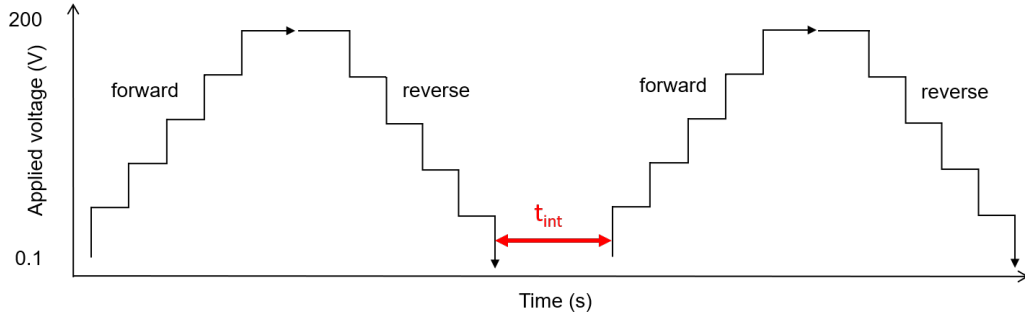


Figure 4.2: Schematic illustration of the continuous (stepwise and steady-state) applied voltage during two subsequent voltage sweeps separated by an interval time (t_{int}) at open-circuit.

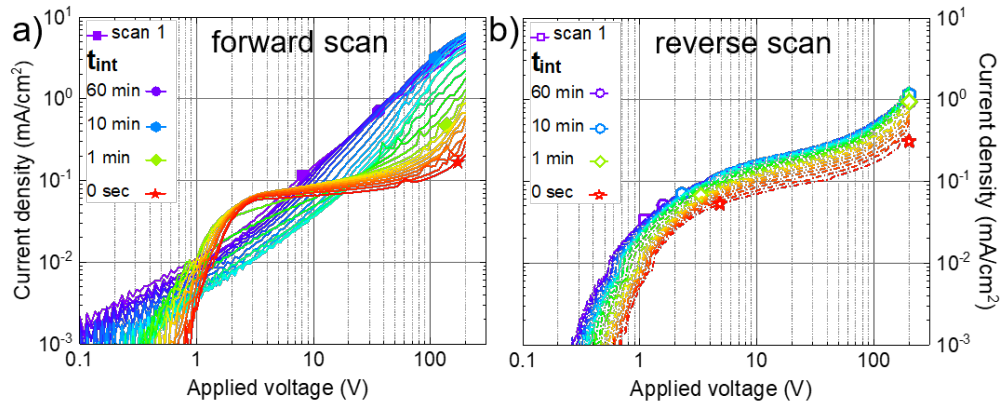


Figure 4.3: Time-dependent hysteresis in SCLC measurements. a) Step-wise change in JV trace during forward scan when changing t_{int} from 60 min to 0 sec.; b) stepwise change in JV trace during the reverse scan when changing t_{int} from 60 min to 0 sec.

electrodes are left floating (at open-circuit) between voltage sweep cycles. During one voltage sweep cycle, a continuously (stepwise and steady state without resting time between voltage steps) increasing electric field is applied from 0.1 to 200 V and back from 200 to 0.1 V. A schematic of the scan routine is depicted in figure 4.2.

The change in hysteresis upon changing t_{int} is shown in figure 4.3, where panels a and b depict the stepwise change in the forward and reverse scans, respectively, when varying t_{int} from 60 min to 0 s in 24 steps. The red and the blue lines in figure 4.5a show the extreme cases for t_{int} equal to 60 min and 0 s, respectively.

“Reproducible hysteresis” is observed in the JV traces, when t_{int} is set to 7 min (green line). Figure 4.4b schematically illustrates the effect of changing t_{int} . All scans are made at a 166 V/s scan speed. Scheme 1 (figure 4.4b) shows that the mobile ions have enough time to diffuse back to their initial position after the voltage sweep if the interval time between two subsequent voltage sweep cycles exceeds the average ionic diffusion time ($t_{\text{ion-diff}}$), i.e. $t_{\text{int}} > t_{\text{ion-diff}}$. In this case, during the forward JV scan of the subsequent voltage sweep, the applied electric field causes a significant change in the position of ions, resulting in the reverse JV scan being significantly different from the forward-direction JV scan, manifesting as large hysteresis (red and green dashed lines in figure 4.4a). Scheme 2 (figure 4.4b) shows that if the interval time before performing the next voltage sweep is smaller than the average ionic diffusion time ($t_{\text{int}} < t_{\text{ion-diff}}$), there is insufficient time for the ions to diffuse back to their initial position before starting the next voltage scan, and the ionic distribution in the film remains predominantly perturbed. In this instance, where $t_{\text{int}} < t_{\text{ion-diff}}$, both the forward and reverse scans (solid and dashed blue lines in figure 4.4a) are very similar and more closely resemble the reverse sweep of the initial scan. This is consistent with the positions of the ions being approximately fixed during the scan but perturbed in comparison with the “unbiased” crystal. Notably, there exists a large current gap at 200 V at the point where the voltage scan direction is switched from forward to reverse when $t_{\text{int}} > t_{\text{ion-diff}}$ (denoted by points I and II in figure 4.4a), whereas this current gap does not exist at 200 V if $t_{\text{int}} < t_{\text{ion-diff}}$ (denoted by points III and IV in figure 4.4a). The current gap is therefore attributed to the fact that there is a finite time (40 ms) taken for the system to start the reverse scan (at 200 V), and a strong forward biasing effect is occurring during this dwell time.

At large forward biases (200 V) the initial current density in the forward direction scan is more than 1 order of magnitude greater than the current density at the same voltage after forward biasing. The forward prebias effect clearly suppresses the current flowing through the crystal. It is expected that the mobile ions diffuse from the bulk

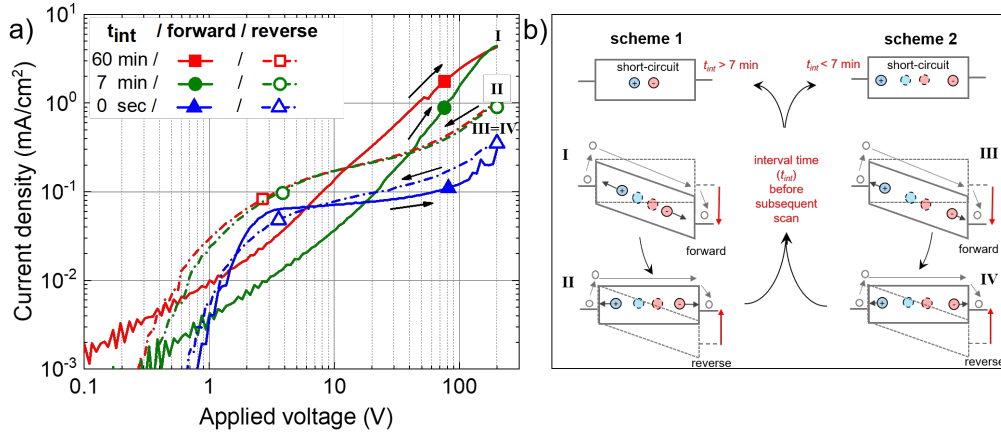


Figure 4.4: Extreme cases of time-dependent hysteresis in SCLC measurements and schematic illustration of mobile ions. a) Large hysteresis between forward and reverse JV traces when $t_{\text{int}} > t_{\text{ion-diff}}$ (red and green lines) and small hysteresis between forward and reverse JV traces when $t_{\text{int}} < t_{\text{ion-diff}}$ (blue line); b) Schematic illustration to explain the difference in hysteresis when $t_{\text{int}} > t_{\text{ion-diff}}$ (scheme 1) and $t_{\text{int}} < t_{\text{ion-diff}}$ (scheme 2). The arrows in situations I-IV in panel b give an indication of the respective distance travelled by ions in each situation. Situations I-IV in panel a are represented by the corresponding illustrations in panel b.

of the perovskite toward the electrodes, when under bias. The suppression of current density may therefore be explained by either the screening of the externally applied electric field to regions near the contacts or a change to the bulk mobility of the perovskite, which may be due to the generation or activation of traps within the perovskite, or a combination of the two.

For the study presented in this chapter, a one-dimensional drift-diffusion model, that includes electrons and holes as well as ionic species, as described in chapter 2.3, is used to verify experiments.^{44–46} In collaboration with V.M. Le Corre *et al.*, it was found that while there is a clear effect of ionic distribution on the simulated JV curves, there is not such a drastic decrease and saturation in the current density in the reverse scan compared to the forward scan as what is observed in the experiment depicted by the green line in figure 4.4a.⁴⁷ A possible explanation could be the creation of an injection barrier next to the electrode when the applied bias is large. This injection barrier could be induced by a number of reasons. For example by degradation of the perovskite

next to the electrode. Another reason could be when the ion density at the electrode interface is large, a thin layer with a different band gap can be formed.⁴⁷ And additionally, literature has reported that ion migration or perovskite-electrode interaction can cause different phases such as PbI_2 next to the electrode, giving rise to such a barrier.⁴⁸

To further understand the role of the prebias effect upon hysteresis, a prebias (+5 or -5 V) is applied for 120 s to the electrodes before performing the JV scans. Figure 4.5a shows reproducible JV curves with little hysteresis upon applying a positive prebias of 5 V, whereas figure 4.5b shows reproducible JV traces with large hysteresis when the polarity of the prebias is switched to -5 V. In panels c and d of figure 4.5, it is schematically illustrated how mobile ions are expected to behave upon applying a positive and negative prebias, respectively. Figure 4.5c represents how positive mobile ions drift toward the carrier injection contact, while negative mobile ions drift toward the opposite electrode, upon applying a positive voltage (1). When the system is back at short circuit, the positive mobile ions are displaced toward the injection contact, while negative mobile ions are displaced toward the other contact (2). When the JV sweep is performed directly after prebiasing, the mobile ions have no time to diffuse away from the interfaces.

Thus, positive and negative ions are displaced toward the electrode interfaces, during both forward (3) and reverse (4) scans. This is in agreement with the small hysteresis in figure 4.5a, because both forward and reverse voltage scan directions are performed under positive prebias conditions. The similarities between figure 4.5a and the blue line in figure 4.4a support the concept of the positive prebias effect as a result of both positive and negative ions separately displacing toward the electrodes. The schematics in figure 4.5d describe how the mechanism is reversed when the polarity of the prebias is switched from positive to negative voltage. Upon application of the negative prebias, negative mobile ions drift toward the electron injection contact, while positive mobile ions drift toward the other contact (1). After going back to short circuit,

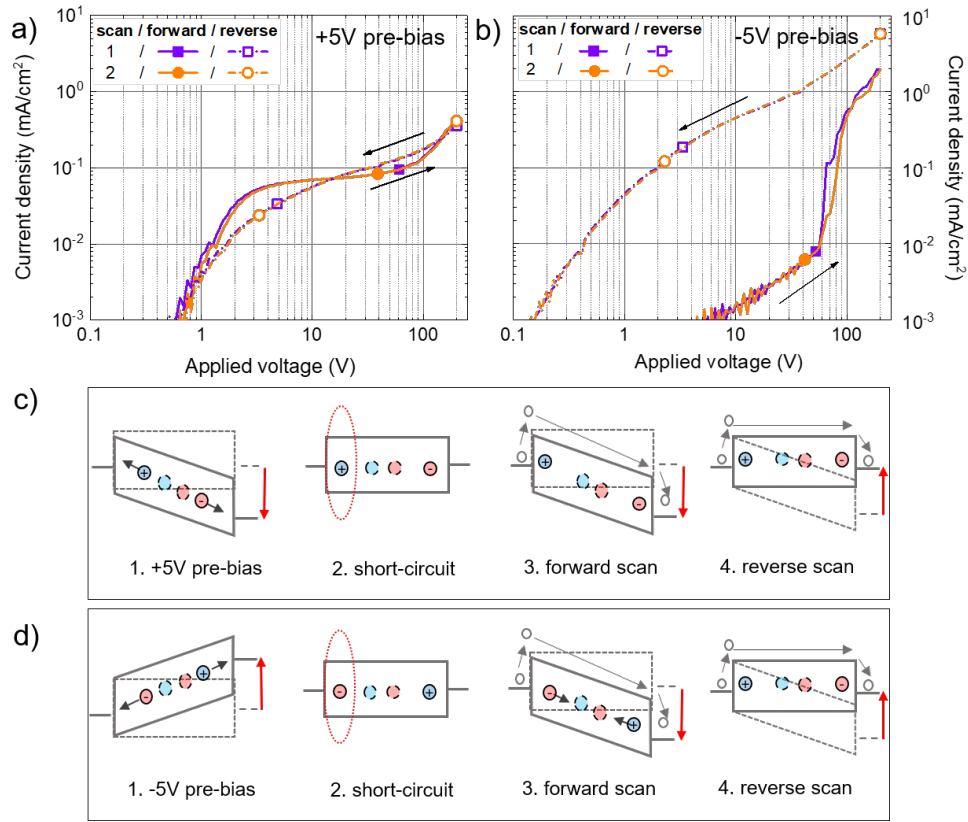


Figure 4.5: Prebias-dependent hysteresis in SCLC measurement and schematic illustration of mobile ions. a) Small reproducible hysteresis in JV traces after applying +5 V prebias (solid and dashed lines for forward and reverse voltage sweep, respectively); b) Large reproducible hysteresis in JV traces after applying -5 V prebias; c) Schematic illustration of selective ion localisation upon applying a positive prebias. A positive prebias causes ion migration toward the electrodes (1). After going back to short circuit, positive ions displaced toward the injection contact (2). Ions remain displaced toward the same electrodes during the forward scan (3) and reverse scan (4); d) Schematic illustration of selective ion localisation upon applying a negative prebias. A negative prebias results in ion migration toward the electrodes (1). After going back to short circuit, negative ions displaced toward the injection contact (2). Ions drift toward the opposite interface during the forward scan (3), as the polarity of the bias condition switches, and stay there during the reverse scan (4). Light blue and red dashed circles represent initial sites of positive and negative ions, respectively. Light blue and red solid circles represent positive and negative ions, respectively.

the respective mobile ions are displaced toward the electrode interfaces (2). During the subsequent forward scan, the bias conditions switch in polarity and mobile ions drift across the crystal toward the opposite electrode (3) with the ionic current, moving in the same direction as the electronic current. During the following reverse JV scan, the mobile ions are again displaced toward the opposite electrode interfaces (4), generating the positive prebias effect during the reverse scan. The switch from a negative to a

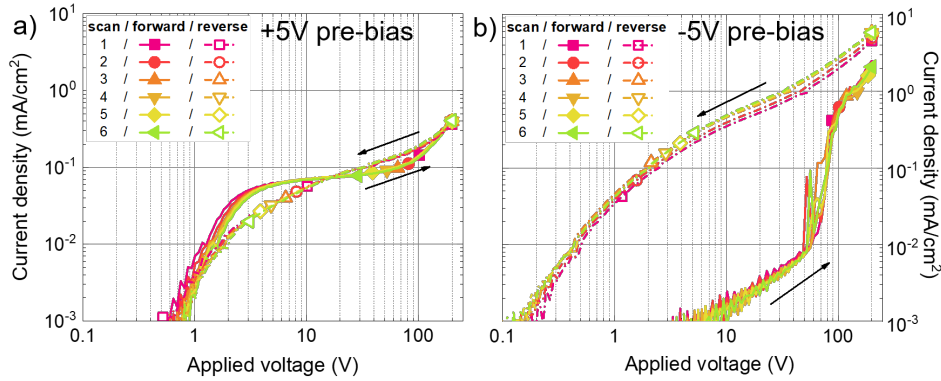


Figure 4.6: Pre-bias dependent hysteresis in SCLC measurements. Reproducibility in JV characteristics from SCLC measurement after applying a) positive pre-bias of +5 V and b) negative pre-bias of -5 V.

positive prebias effect during the voltage sweep corroborates with the observed large hysteresis, as shown in figure 4.5b. Figure 4.6 depicts the reproducibility of the JV traces when the ions are displaced toward the electrode interfaces. It is important to note that all continuous stepwise voltage measurements have been performed on the same device in the dark under vacuum (10^{-4} mbar) at room temperature. Although this chapter identifies the origin of the positive (negative) prebias effect, and therefore the root of hysteresis, the net displacement of ionic charge and a perturbation of the electric field through the crystal will still effect the charge carrier injection and electronic conductivity. This makes it difficult to determine physical properties from the measurement. Therefore, this chapter devises a measurement protocol which circumvents the influence of mobile ions.

4.3.3 Pulsed Voltage Space-Charge Limited Current Measurements

In this section, a well-defined transient pulsed voltage in the SCLC measurement is introduced, with an extreme difference between measurement time and rest time, to obtain accurate current- voltage curves from SCLC measurements without redistributing mobile ions through the single crystal while measuring. Transient current

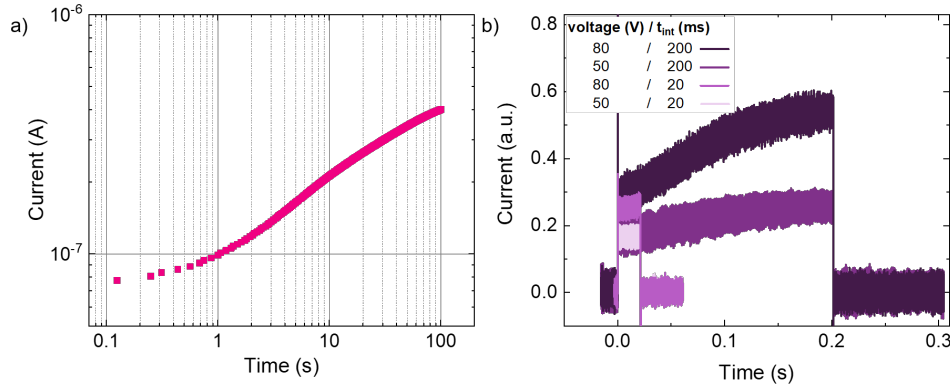


Figure 4.7: Transient current measurement while applying a voltage to the device. a) Current while applying 10 V to the device. The measurement shows that during the short pulse (20 ms) the mobile ions do not affect the current up to few hundred ms; b) Current while applying 50 and 80 V for 20 and 200 ms integration time, respectively. The measurement shows that the system is unperturbed during a short voltage pulse of 20 ms integration time.

measurements (shown in figure 4.7a) show that it is possible to hold a fixed voltage across the crystal for more than 100 ms, before the current flow through the device begins to be perturbed, presumably by ionic redistribution. To further ensure this, the current is measured as a function of time for both 20 and 200 ms integration time, as shown in figure 4.7b. A 20 ms integration time for voltage pulses is short enough for accurate electronic current measurements during the PV-SCLC measurement. Therefore, a voltage pulse width of 20 ms is applied, and the time between voltage pulses (t_{bvp}) is set to 7 min, which was previously determined to be the average ionic redistribution time after one voltage sweep.

By going back to short circuit during t_{bvp} , the mobile ions diffuse back to their initial position after every voltage pulse, and thereby the prebias effect is eliminated. Figure 4.8a (1) shows a schematic of this pulsed voltage measurement, and the respective ion position is depicted in figure 4.8a (2). Figure 4.8b shows the resulting JV curves from MAPbBr₃ single crystals with different thicknesses. When t_{bvp} is set to be larger than $t_{ion-diff}$ during the SCLC measurement, as is the case for $t_{bvp} = 7$ min, reproducible, nonhysteretic JV characteristics are obtained from all single crystals. The lack of hysteresis is consistent with the ions remaining localised in their original positions,

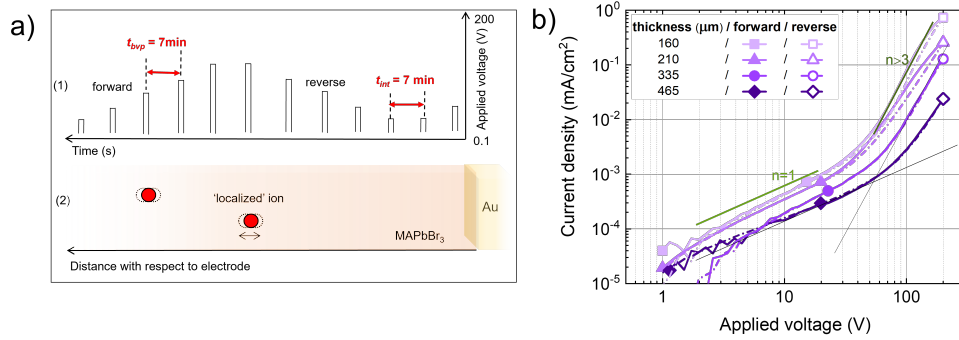


Figure 4.8: Thickness-dependent PV-SCLC measurement. a) Schematic illustration of the PV-SCLC measurement (1) and the respective 'localised' ion motion (2). Both t_{bvp} and t_{int} are set to 7 min during the PV-SCLC measurement; b) Thickness-dependent JV traces without hysteresis extracted from the PV-SCLC measurement.

or close enough so as not to significantly perturb the JV characteristics, during the short voltage pulses of the measurement. Additionally, there is no sign of degradation, which confirms the hypothesis that the accumulation of ions at high voltages gives rise to an injection barrier that can limit the current.

V.M. Le Corre *et al.*, have used drift-diffusion modelling to show that the PV-SCLC approach is fully justified (for both single crystals and thin films), and that ions do not move significantly and have little to no influence on the current at such a time scale and electric field, by simulating the pulsed measurement.⁴⁷

The voltage range of the measurement instrument limits the possibility of measuring all possible regimes of a typical SCLC measurement for all thicknesses; in particular, it is not possible to access the MG regime which is equivalent to trap-free SCLC (corresponding to all traps in the material being filled). Drift-diffusion simulations, as discussed in chapter 2.3, allow for an estimation of the mobility when the SCLC regime is not reached. Nevertheless, the current range studied in this chapter reveals a rich variety of characteristics. All thicknesses show a clear Ohmic region ($J \propto V^{n=1}$) at low voltages, from which the conductivity (σ) can be determined following $\sigma = \frac{L}{A} \frac{1}{R}$, where L is the thickness of the crystal, A the area, and R the

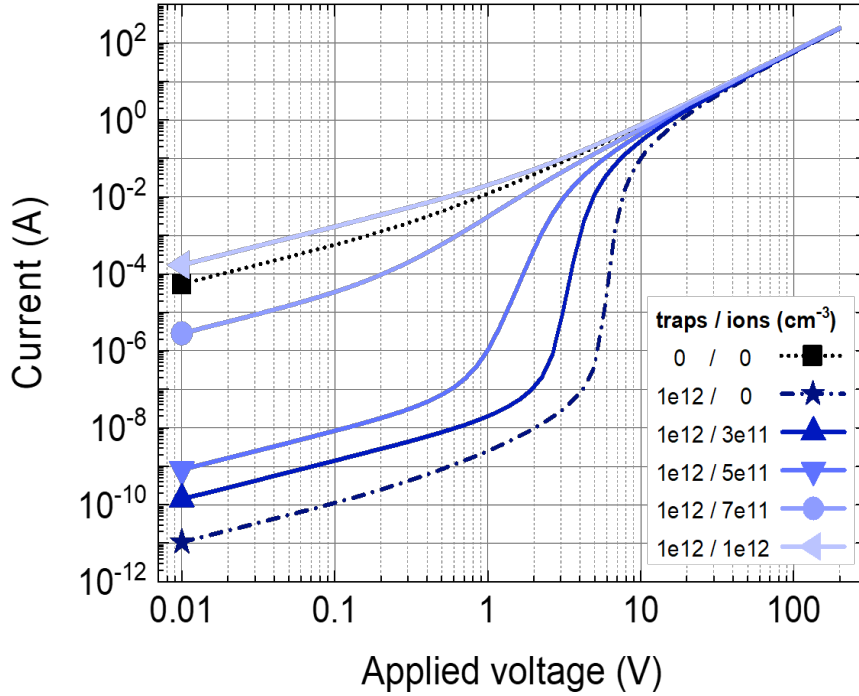


Figure 4.9: Simulated current-voltage characteristics during pulsed voltage SCLC measurements. Modeled IV curve for a $170\ \mu\text{m}$ electron-only device with trap states and mobile ions. V_{ons} shifts to lower voltages when an ion density which is lower than, but within an order of magnitude of the trap density, is added to the system. The ion density consists of both positive and negative ions in equal density. If the ion density is equal to, or greater than, the trap density, the effect of traps is strongly overshadowed by the ions.

resistance. The conductivity is calculated to be $6.9 \pm 0.3 \times 10^{-10}\ \text{Scm}^{-1}$. This is about 1 order of magnitude lower than previously reported conductivity values extracted from SCLC measurements on single crystals.^{23,30} This is in agreement with results that the electron current is influenced by the ionic conduction, as previously explained and shown in figure 4.4 and figure 4.7. Chapter 5 will go into more detail on the low-voltage regime of SCLC measurements. After the Ohmic regime, a gradual increase in gradient is observed in the JV characteristics and a transition into the $n \geq 3$ region, because of the filling of trap states with increasing electric field. V_{ons} for 160, 210, 335, and $465\ \mu\text{m}$ thick crystals is extracted to be 48, 49, 70, and 91 V, respectively.

4.3. Results and Discussion

Table 4.1: Parameters used in the device simulation to investigate the correlation of mobile ions and trap states.

Parameter	Symbol	Value	Reference
Perovskite bandgap	E_{gap}	2.2 eV	49
Effective density of states	N_C	$2.5 \times 10^{18} \text{ cm}^{-3}$	guess
Relative permittivity	ϵ_r	25.5	50
Mobility	μ	$1 \text{ cm}^2(\text{Vs})^{-1}$	guess
Electron injection barrier	ϕ_a and ϕ_c	0.2 eV	guess

To assess whether equation 2.35 can be used to estimate trap densities from V_{ons} , numerical simulations (as described in chapter 2.3) are performed to gauge the influence of ionic species on SCLC measurements.^{44–46} The simulations mimic the pulsed voltage measurements by first calculating the ionic distribution at zero voltage and then sweeping the voltage while keeping the ions fixed. Table 4.1 shows the fit parameters used for this study. This procedure recreates current-voltage (IV) measurements without redistributing mobile ions throughout the crystal. In the absence of ions, the simulated IV characteristics indeed show a voltage regime that corresponds to the filling of traps, as shown by the dashed line in figure 4.9. However, mobile ions also contribute space-charge in the bulk of the crystal, effectively negating the charge of trapped electrons. As more ions are introduced, V_{ons} shifts to lower voltages, and eventually the effect of traps disappears, as shown in figure 4.9). Equation 2.35, therefore, yields only a lower limit of the trap density, and if the ion and trap densities are within the same order of magnitude, should be rewritten in terms of net charged in the bulk such as:⁴⁷

$$V_{\text{net}} \approx \frac{en_t L^2}{2\epsilon_0 \epsilon_r} \approx \frac{e(n_t - n_{\text{ion}}) L^2}{2\epsilon_0 \epsilon_r} \quad (4.1)$$

Similarly, equation 2.54 in chapter 2 can be expressed in terms of the net charge in the bulk. Equation 4.1 still holds when other types of charges such as dopants are added. In that case, $V_{\text{net}} = n_t - n_{\text{ion}} + N_A - N_D$, where N_A and N_D are acceptors and

donors, respectively. Crucial for the interpretation of SCLC measurements is that the net charge in the bulk of the perovskite is measured. For example, if more than one type of trap is considered, with both some additional donor and acceptor states, n_t in equation 4.1 (and 2.35) corresponds to the net charge of all traps.

While equation 2.35 underestimates the number of traps if there are mobile ions, the simulations also show that traps dominate (i.e., outnumber mobile ions) if V_{ons} can be observed. More specifically, this assumes the case where the traps are negatively charged when filled with electrons, and the ion density consists of positive and negative ions in equal density. Moreover, the simulated IV curves reveal that V_{ons} reduces by only up to 1 order of magnitude before it is indeterminable. In other words, equation 2.35 underestimates the density of the trapped carriers because of the presence of ions by no more than 1 order of magnitude. It is important to emphasise that in order to quantify the actual trap density, the distribution of traps should be known.¹⁵ As explained in chapter 2, the trap-filling regime is conventionally modelled on a single trap level, where it is expected to observe a rapid increase in current density with increasing applied bias, as the trap-filling onset voltage is passed, whereas a broader trap distribution results in a more gradual rise in current after V_{ons} . From the gradual rise in current after V_{ons} , it is only possible to attribute a lower bound to the trap density from the V_{ons} . It is also important to note that specifically the density of trapped carriers is determined at this specific voltage point, rather than the total density of traps. In this case, this is equal to $2.8 \pm 1.8 \times 10^{12} \text{ cm}^{-3}$. After all the trap states are filled, it should be possible to measure the bulk properties in the single crystals, as the space-charge limited regime in the absence of traps, where $J \propto V^{n=2}$, is entered. However, as mentioned earlier, even for the thinnest crystals that have been studied here, this regime is not conclusively entered within the voltage range of the measurement. Hence, the SCLC charge carrier mobilities for the samples that are studied in this chapter have not been determined.

4.4 Conclusion and Outlook

This chapter discussed how mobile ions can have a dramatic effect on electronic current extraction during SCLC measurements, masking the underlying fundamental electronic properties of the semiconductor. To circumvent this, a pulsed voltage space-charge limited current measurement methodology is introduced, which diminishes the motion of mobile ions. This allows to obtain JV curves without hysteresis from semiconductors that exhibit both ionic and electronic conductivity. The results presented from this revised voltage scanning protocol finally resolve the ambiguities that surround similar electronic measurements of metal halide perovskite single crystals. The established method allows to accurately measure the electronic properties and trap characteristics, without perturbation in the electronic current flow by the motion of mobile ions. From the resulting JV traces, a lower bound trap density in MAPbBr₃ single crystals of $2.8 \pm 1.8 \times 10^{12} \text{ cm}^{-3}$ is calculated. The aim of this chapter is also to highlight that in order to accurately interpret perovskite-based device measurements and achieve comparability between different laboratories, the experimental conditions and analysis routines should be clearly described and carefully conducted because of the combined ionic and electronic nature of perovskites. More accurate measurements of the fundamental properties of these materials should ultimately lead to more effective development of their optoelectronic devices.

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Dark Current-Voltage Characteristics in Metal Halide Perovskite Single Crystals

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E.A. Duijnste^a, V.M. Le Corre^b, M.B. Johnston^a, L.J.A. Koster^{b*}, J. Lim^{c*} H.J. Snaith^{a*}, Understanding Dark Current-Voltage Characteristics in Metal-Halide Perovskite Single Crystals, *Physical Review Applied*, 15, 014006-1-014006-7, 2021. Copyright 2022 American Physical Society.

5.1 Context and Summary

Hybrid halide perovskites have great potential for application in optoelectronic devices. However, as highlighted in chapter 2 and 4, an understanding of some basic properties, such as charge-carrier transport, remains inconclusive, mainly due to the mixed ionic and electronic nature of these materials. In this chapter, temperature-dependent pulsed-

voltage space-charge-limited current measurements (a measurement methodology that is introduced in chapter 4) are reported and analysed to provide a detailed look into the electronic properties of methylammonium lead tribromide (MAPbBr₃) and methylammonium lead triiodide (MAPbI₃) single crystals. It is shown here that the background carrier density in these crystals is orders of magnitude higher than that expected from thermally excited carriers from the valence band. The complexity of the system is highlighted via a combination of experiments and drift-diffusion simulations and it is shown that different factors, such as thermal injection from the electrodes, temperature-dependent mobility, and trap and ion density, influence the free-carrier concentration. Via experiments, the effective activation energies for conductivity are determined to be 349 ± 10 meV for MAPbBr₃ and 193 ± 12 meV for MAPbI₃, which includes the sum of all of these factors. It is also pointed out here that fitting the dark JV curve with a drift-diffusion model allows for the extraction of intrinsic parameters, such as mobility and trap and ion density. From simulations, a charge-carrier mobility of $12.9 \text{ cm}^2/\text{Vs}$, a trap density of $1.52 \times 10^{13} \text{ cm}^{-3}$, and an ion density of $3.19 \times 10^{12} \text{ cm}^{-3}$ for MAPbBr₃ single crystals is determined. The insights into charge-carrier transport in metal-halide perovskite single crystals that are reported here will be beneficial for device optimisation in various optoelectronic applications.

5.2 Introduction

Metal-halide perovskites are prospective candidates for facilitating not only third-generation solar cell technologies,^{1–3} but also other applications, such as solid state lasers,^{4,5} light-emitting diodes,⁶ and radiation detectors.⁷ As discussed in chapter 2 and 4, it is widely known that perovskites possess, apart from electronic conductivity, ionic conductivity, where mobile ions can shield the bulk material from externally applied biases.^{8–10} In this regard, electronic charge-carrier dynamics can be strongly influenced by the existence of drifting and diffusing mobile ions, which makes the use of traditional electrical characterisation techniques questionable and limits information

available about temperature-dependent charge-carrier density and factors influencing electronic conductivity in perovskites, so far.¹¹ The dark electronic conductivity in perovskite single crystals via temperature-dependent PV-SCLC measurements is studied here.^{11,12} As explained in chapter 4, during the PV-SCLC measurement, the voltage pulse is short, such that the induced ion motion is minimised and the waiting time between subsequent voltage pulses is sufficient for the system to relax back to its initial conditions after every bias pulse. It should be noted that, even though the influence of mobile ions is overcome, and hence do not need to be accounted for, the presence of static ionic charge density still strongly influences the JV characteristics, and is hence accounted for in the characterisation and subsequent modelling.¹¹ Despite the fact that more accurate numerical approaches are available,^{13–17} the JV curves for a semiconductor with traps, extracted from SCLC measurements, are typically subdivided into three distinct regions if a number of assumptions, which will be discussed below, are valid. Details of these regions are discussed extensively in section 2.66 in chapter 2, but iterated briefly here.

First is the Ohmic regime (1), where the current rises linearly with the voltage. Conventionally, Ohm's law (see section 2.1.1.3 and section 2.1.3.1 in chapter 2) is only valid if the thickness of the semiconductor is more than double the Debye length, such that the current is only driven by the drift of charge carriers.¹⁵ If this is not the case, and the space-charge region from both contacts overlap, the overall charge density is increased. The low-voltage current density then follows the "moving electrode" equation rather than Ohm's law, which equals:

$$J = 4\pi^2 \frac{\mu kT}{e} \epsilon_0 \epsilon_r \frac{V}{L^3} \quad (5.1)$$

In this case, the departure from Ohm's law is thickness independent and occurs at the cross-over point V_X :

$$V_X = \frac{32\pi^2}{9} \frac{kT}{e} \quad (5.2)$$

At room temperature, V_X is around 0.9 V.^{15,18–21}

After region (1), there is the onset voltage (V_{ons}), after which the slope (equation 2.24 in chapter 2), in the JV curve is larger than two due to the filling of trap states (2). It is important to note that this region will only occur if the traps are negatively charged when filled with an electron.

To clarify that statement, the correlation of ionic defects to trap states in single crystals is shown by simulating the JV characteristics of the pulsed voltage space-charge limited current measurement (PV-SCLC) measurements (see Chapter 4) for a 10 μm thick electron-only device with the device model described in chapter 2.3.

Figure 5.1a and b show the JV curves of two scenarios in the absence and presence of ionic species: (a) neutrally charged traps when filled with electrons and (b) negatively charged trap states when filled with electrons. Table 5.1 shows the fit parameters used for these simulations. Figure 5.1a. shows that the current-density is simply linear at low voltages, if the traps are assumed to be neutral when filled with electrons. If the same density of ions as neutral traps is implemented, the current-density remains linear at the low voltages, but because of an increase in net space charge increases, the current-density increases. Figure 5.1b. shows a sharp inflection point in current-density at the onset voltage if the traps are assumed to be negatively charged with electrons. For comparison, it is shown that the sharp onset disappears if the same density of traps and ions is implemented in the active layer. Thus, when the experimental data shows an actual slope larger than two, it means that within the single crystal there are dominantly sites that are negatively charged when filled with electrons.

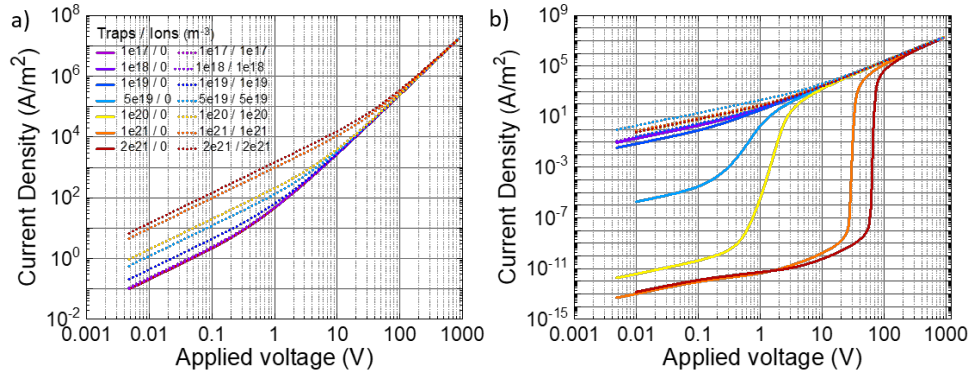


Figure 5.1: Simulated JV curve for an electron-only device with a) neutrally charged trap states when filled with electrons, and b) negatively charged trap states when filled with electrons. The sharp onset of conductivity only occurs when the traps are neutral when filled with electrons.

Table 5.1: Parameters used in the device simulation to investigate the correlation of mobile ions and trap states which are either neutral or charged when filled with electrons

Parameter	Symbol	Value	Reference
Perovskite bandgap	E_{gap}	2.2 eV	22
Effective density of states	N_C	$2.5 \times 10^{18} \text{ cm}^{-3}$	guess
Relative permittivity	ϵ_r	24.1	23
Mobility	μ	$1 \text{ cm}^2(\text{Vs})^{-1}$	guess

Under certain specific conditions,^{11,14,24} the number of trapped carriers in the material can be calculated from this onset voltage. However, in chapter 4, it was shown that ions, which are likely to exist in perovskites, contribute to the space charge in the bulk of the crystal, and thereby effectively negate the charge of trapped electrons.¹¹ Additionally, it is very likely that traps are induced with thermal energy, and therefore extracting the trapped carrier density via the onset voltage is rather complicated. Lastly, when all traps are filled, the drift current-density profile for a single carrier device is assumed to follow the MG law (3), where the current density is proportional to the voltage squared.²⁵ Röhr *et al.* show that there is only a very limited number of cases where the conductivity and mobility can be determined by

evaluating the MG law at high voltages and Ohm's law at low voltages.¹⁵

Here, methylammonium lead tribromide (MAPbBr₃) and methylammonium lead triiodide (MAPbI₃) single crystals of various thicknesses are grown and prepared. The experimental details are discussed in section 3.1 in chapter 3. Both single crystals are studied, where the screening effects of migrating ions on electrical conductivity are diminished by temperature-controlled PV-SCLC measurements. Via temperature-dependent PV-SCLC measurements it is shown that, for both crystal types, a decrease in conductivity in regime (1) and an increase in onset voltage and slope in region (2) upon reducing the temperature is observed. A detailed insight via experiments and drift-diffusion simulations is provided into how a combination of multiple factors, including injection barrier, temperature-induced trap states, and ionic species, and a change in mobility, can affect the JV curves and explain the background carrier density. Importantly, these factors complicate the use of SCLC theory, and an awareness and understanding of the charge-carrier density is very useful knowledge for the further development of device performance.

5.3 Results and Discussion

5.3.1 Intrinsic Carrier Density

The basics of an intrinsic semiconductor, in which the Fermi level, E_F lies in the middle of the band gap, are described schematically in figure 2.2 in chapter 2. The intrinsic carrier-density, n_i , in the conduction band, due to thermal population of carriers from the valence band, can be calculated using equation 2.15. For MAPbBr₃, the effective electron mass, m_n^* , equals $0.234 m_n$,²⁶ such that N_C equals $2.77 \times 10^{18} \text{ cm}^{-3}$ at room temperature. For comparison, MAPbI₃ has an m_n^* of $0.208 m_n$,²⁶ and therefore, N_C is $2.32 \times 10^{18} \text{ cm}^{-3}$ at room temperature. From this, and the 2.3- and 1.6-eV wide band gap of MAPbBr₃ and MAPbI₃, respectively,²⁶ the thermal population of carriers

in the conduction band as a function of temperature can be calculated, as depicted in figure 5.2a.

At room temperature, this would imply that, if perovskite single crystals were not extrinsically doped, their thermal population in the conduction band at room temperature would equal 6.00×10^{-2} and $4.09 \times 10^4 \text{ cm}^{-3}$ for MAPbBr₃ and MAPbI₃, respectively. Notably, N_C is proportional to $T^{1.5}$, and thus, only changes by slightly more than one order of magnitude over a temperature range from 50 to 2000 K. The community is, however, often under the wrong assumption that the extracted background carrier density in the low-voltage regime (1) is the intrinsic carrier density, which is explicitly the thermal population from the valence band.

5.3.2 Pulsed-Voltage Space-Charge Limited Current Measurement

In figures 5.2c and 5.2d the JV characteristics from temperature-dependent PV-SCLC measurements of both MAPbBr₃ and MAPbI₃, respectively, are depicted. Similar trends for multiple thicknesses are shown in Figures 5.3a,b and 5.4a,b, for MAPbBr₃ and MAPbI₃, respectively.

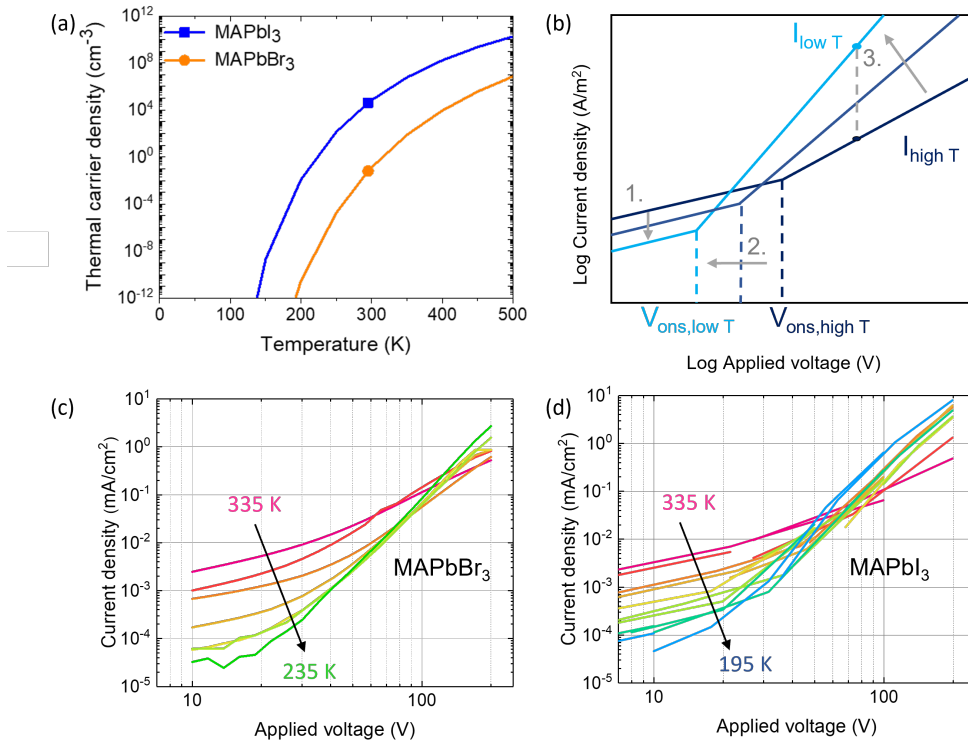


Figure 5.2: Thermal carrier population in the conduction band and temperature-dependent PV-SCLC measurements. a) Thermal carrier population in the conduction band as a function of temperature. The orange line represents the density for an intrinsic semiconductor with a 2.3 eV band gap and the blue line a 1.61 eV wide band gap; b) Schematic of JV characteristics of the temperature-dependent PV-SCLC measurement, where region (1) indicates the decrease in conductivity; region (2) is the shift of the onset voltage; and region (3) is the increase in slope in the trap-filling regime upon decreasing the temperature; Temperature-dependent PV-SCLC measurements of c) MAPbBr₃ (335 to 235 K in steps of 20 K); d) MAPbI₃ (335 to 195 K in steps of 20 K).

All device types, dimensions, and their respective properties used in this study are given in Table A.1 in Appendix A. Because MAPbBr₃ undergoes its first phase transition from cubic to tetragonal at around 220 K, the temperature is varied from 335 to 235 K.²⁷ For MAPbI₃, it is possible to go to slightly lower temperatures (195 K), as it transitions from the tetragonal to orthorhombic phase at around 160 K.²⁸ For both crystals, the temperature is changed in steps of 20 K, and the characteristics of the JV curve that are most influenced by temperature are identified. In figure 5.2b, a schematic indicating the three different regions in the JV characteristics that occur upon lowering the temperature are shown: (1) represents the decrease in the low-voltage Ohmic regime, (2) indicates the shift in the onset voltage towards lower

5.3. Results and Discussion

voltages upon reducing the temperature, and (3) represents the increase in the slope of the JV curve at voltages larger than the onset voltage. Sections 5.3.2-5.3.5 elaborate further on this.

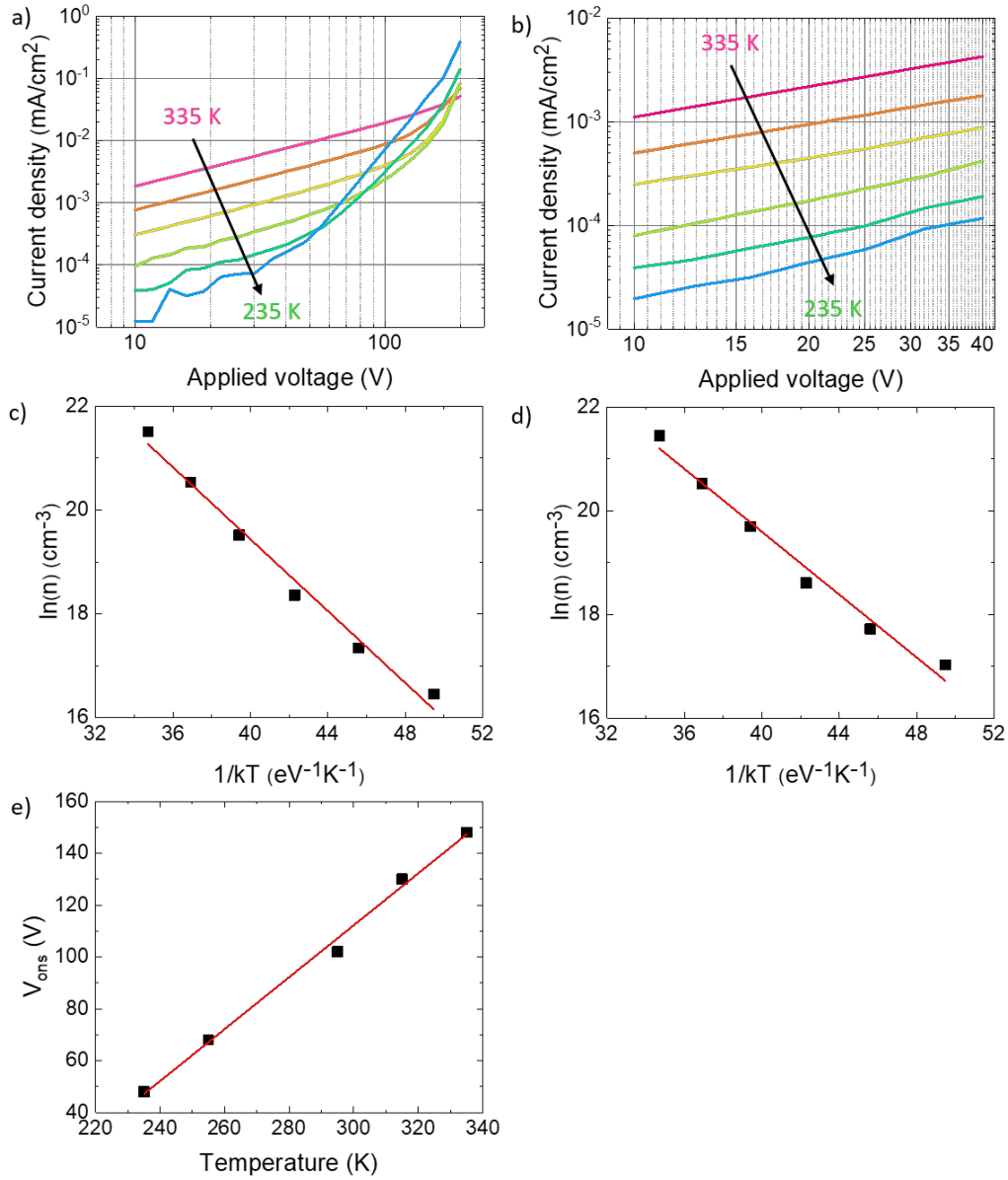


Figure 5.3: PV-SCLC measurement and respective properties for MAPbBr₃. a) and b) PV-SCLC measurements for a 210 μm and 335 μm thick crystal, respectively, at different temperatures, ranging from 335 K to 235 K in steps of 20 K; c) and d) natural logarithm of the carrier density as a function of 1/kT for a 210 μm and 335 μm thick crystal, respectively; e) V_{ons} as function of temperature for a 210 μm thick crystal.

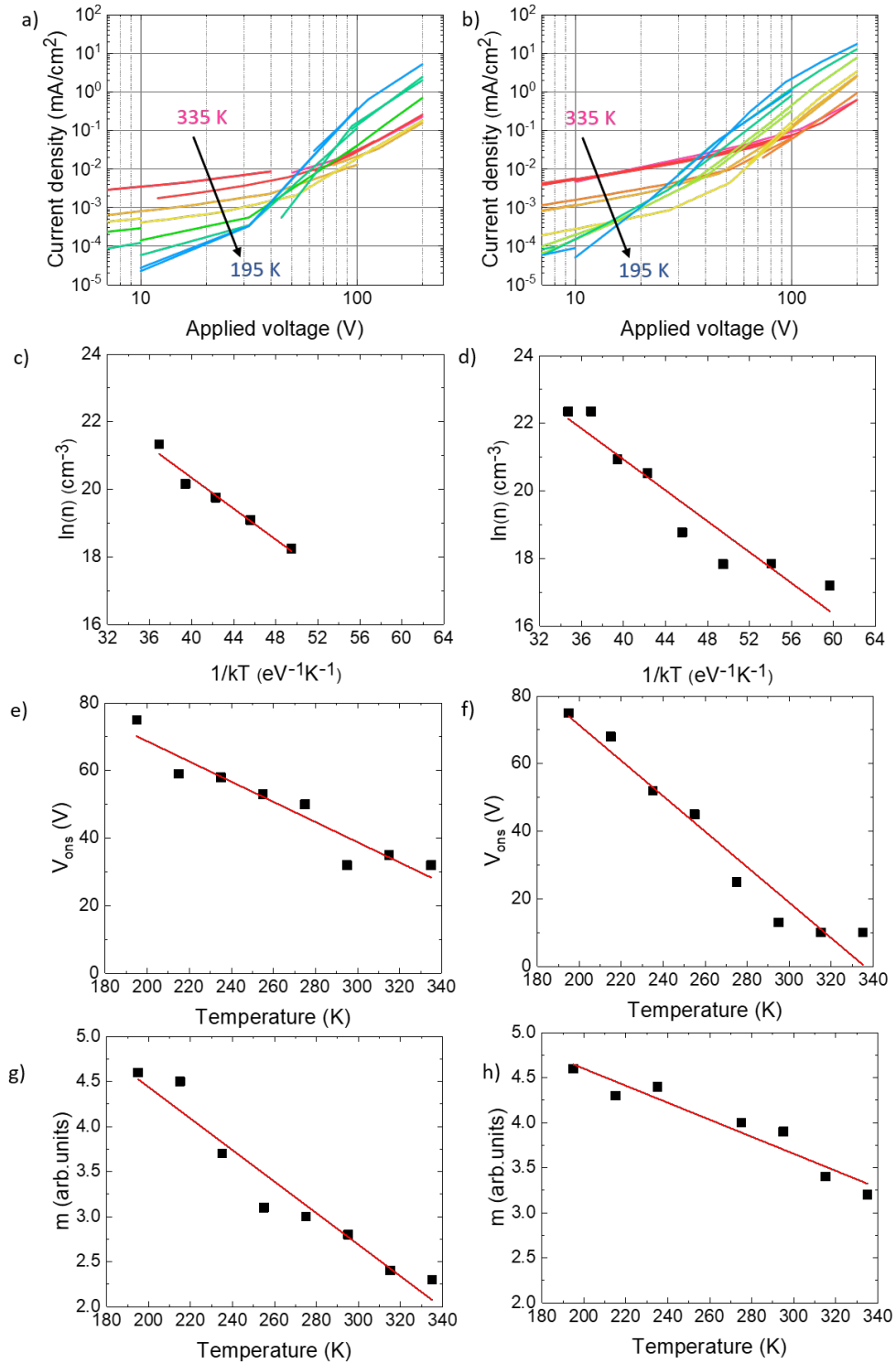


Figure 5.4: PV-SCLC measurement and respective properties for MAPbI₃ a) and b) PV-SCLC measurements for a 240 μm and 290 μm thick crystal, respectively, at different temperatures, ranging from 335 K to 195 K in steps of 20 K; c) and d) natural logarithm of the carrier density as a function of $1/kT$ for a 240 μm and 290 μm thick crystal, respectively; e) and f) V_{ons} as function of temperature for a 240 μm and 290 μm thick crystal, respectively; g) and h) m as function of temperature for 240 μm and 290 μm thick crystal, respectively.

5.3.3 Background Carrier Density

From the Ohmic region (1) in the JV curves, a dark dc conductivity of $(1.02 \pm 0.03) \times 10^{-7} \text{ Sm}^{-1}$ for a $160\text{-}\mu\text{m}$ -thick MAPbBr_3 crystal and $(4.43 \pm 0.98) \times 10^{-7} \text{ Sm}^{-1}$ for a $280\text{-}\mu\text{m}$ -thick MAPbI_3 crystal at room temperature is calculated. Via transient photoconductivity (TPC) measurements,²⁹ a sum of mobilities is extracted at room temperature of $(27 \pm 1) \text{ cm}^2/\text{Vs}$ in MAPbBr_3 and $(45 \pm 3) \text{ cm}^2/\text{Vs}$ in MAPbI_3 . The sum mobilities at different fluences is depicted in figure 5.5.

In this study, it is assumed that the electron and hole mobility are similar. It has been previously shown that the Hall mobility exhibits an inverse power-law temperature dependence in the cubic phase. Using the power exponent, $\mu \propto T^{-1.5}$,^{30–32} the mobility values of the MAPbBr_3 crystals at all measured temperatures are calculated, with respect to room-temperature-measured mobility.

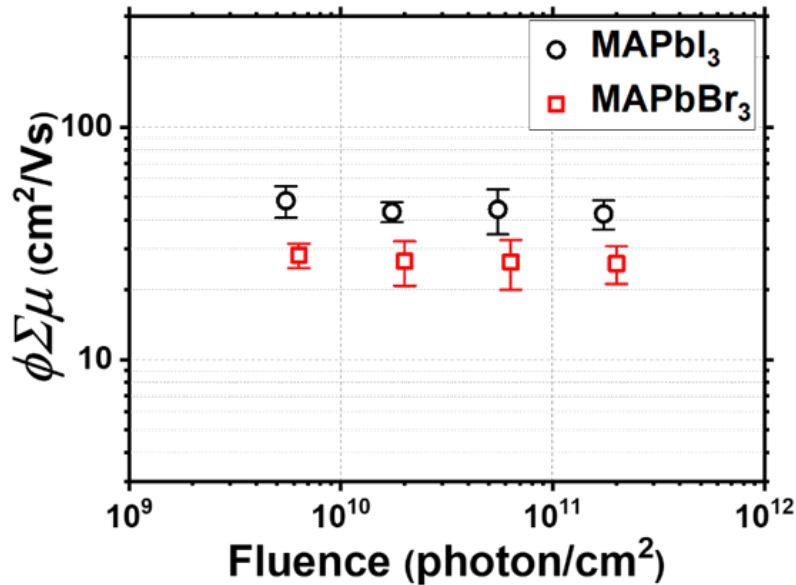


Figure 5.5: Evaluation of long-range mobility of perovskite single crystals by transient photoconductivity measurements. It shows the sum of mobilities ($\Sigma \phi \mu$), multiplied by the fraction of absorbed light which generates mobile free-carriers (ϕ), of electrons and holes as a function of fluence. These measurements have been done together with collaborator Prof. J. Lim and M. Kober-Czerny

By applying equation 2.17, n is determined to be equal to $4.76 \times 10^8 \text{ cm}^{-3}$ for MAPbBr_3 and $1.24 \times 10^9 \text{ cm}^{-3}$ for MAPbI_3 at room temperature. Figure 5.6 shows that the background carrier density is orders of magnitude higher than the intrinsic carrier density (solid lines) calculated from thermodynamics. Using $\mu \propto T^{-1.5}$, it is possible to determine the carrier density at all measurement temperatures and this is plotted in figure 5.6. As shown by the solid circles and squares, there is an expected increase in carrier density with increasing temperature. From this Arrhenius relation, an effective activation energy ($E_{a,\text{eff}}$) of $(349 \pm 10) \text{ meV}$ for MAPbBr_3 and $(193 \pm 12) \text{ meV}$ for MAPbI_3 , is calculated. Notably, this effective activation energy is much higher than that of, for example, doped silicon, where the low ionization energy of ionizable donor or acceptor states is usually very close to the band edge. The processes governing this Arrhenius relation is further elaborated on in section 5.3.5 with the help of drift-diffusion simulations. The dashed lines in figure 5.6 represent the calculated carrier density in the conduction band, extracted from conductivity data, as a function of the reciprocal temperature. These results clearly show that, over the temperature range of these measurements, this is very far from the intrinsic range and the carrier density in the conduction band is governed by other processes that are discussed in section 5.3.5.

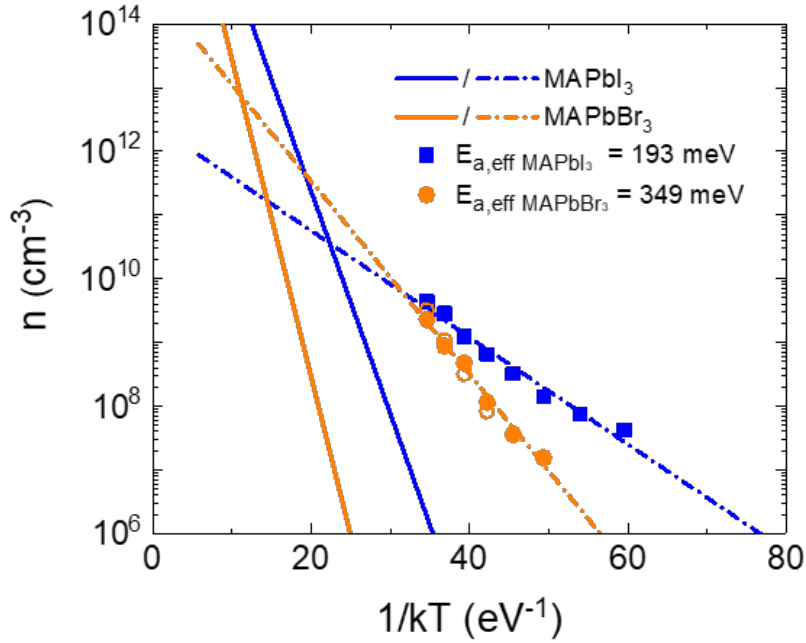


Figure 5.6: Carrier density in the conduction band as a function of the reciprocal temperature for MAPbBr₃ (orange) and MAPbI₃ (blue). Solid lines indicate the intrinsic carrier density calculated from equation 2.15. Solid circles and squares are carrier densities estimated from experimental conductivity measurements. From this Arrhenius relationship, extrinsic carrier density in the conduction band is calculated, as indicated by the dashed lines. Numerical simulations (open circles) show carrier density in the bulk of the MAPbBr₃ single crystal (far away from the charge-injection electrodes). The numerical fitting was done by collaborator Dr. V.M. Le Corre.

5.3.4 Ionic Space Charge and Trap States

A departure from the Ohmic regime is observed at the onset voltage, and figure 5.7a shows that this onset voltage shifts towards lower values upon reducing the temperature. Additionally, there is a linear relation between the slope (m) of the $\log(J)$ - $\log(V)$ characteristics of the trap-filling regime as a function of temperature, as depicted in Figure 5.7b. The variation of n , V_{ons} , and m for MAPbBr₃ and MAPbI₃ crystals of different thicknesses is shown in Figs. 5.3c-e and 5.4c-h, respectively.

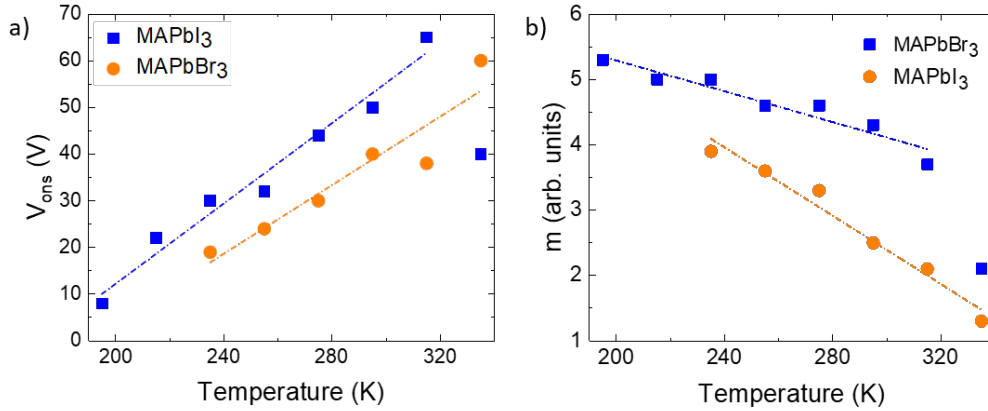


Figure 5.7: Temperature-dependent onset voltage and slope; a) The onset voltage, V_{ons} , and b) the slope, m , as a function of temperature. Conventionally, it is assumed that the onset voltage indicates that the injected electrons are significantly filling the defect states in the band gap, and the slope with which the current-density increases after the onset voltage can be used to determine the trap distribution. However, the mixed ionic-electronic nature of the perovskite, makes it ambiguous to quantitatively describe the change in slope and extract the trap density from the onset voltage. The increase in onset voltage points towards an increase in trap density with increasing temperature.

Conventionally, it is assumed that the JV characteristics start to deviate from being linear when the injected electrons are significantly filling the defect states in the band gap, and the slope with which the current density increases after the onset voltage can be used to determine the trap distribution.^{33,34} However, as explained in chapter 4, if the density of ionic space charge (which is static) is within the same order of magnitude as that of the density of defect states, the onset voltage shifts and the slope is affected, thereby making it ambiguous to quantitatively describe the change in slope and extract the trap density from the onset voltage.¹¹

5.3.5 Drift-Diffusion Simulations

To pinpoint which effects govern the higher-than-expected intrinsic charge-carrier density, the effective activation energy, and the change in V_{ons} and m , the JV characteristics are numerically simulated using a one-dimensional drift-diffusion model that includes electrons and holes as well as ionic species. These simulations were done in collaboration with Dr. V.M. Le Corre. Notably, the ionic species are static for the simulations. This modelling methodology is used to extract trap and ion densities,

and mobility over a range of temperature. Details on the device model are given in chapter 2.3. The simulation mimics the PV-SCLC measurements by first calculating the ionic distribution at 0 V, and then sweeping the voltage, while keeping the ions fixed. In this way, the IV measurements are recreated without redistributing the mobile ions through the crystal. Firstly, the dark JV curve at room temperature is fitted, as shown in Figure 5.8a, from which an electron mobility of $12.9 \text{ cm}^2/\text{Vs}$, a trap density (n_t) of $1.52 \times 10^{12} \text{ cm}^{-3}$, and an ion density (n_{ion}) of $3.19 \times 10^{12} \text{ cm}^{-3}$ is extracted. This mobility is in very close agreement with the sum of mobilities that is determined from the TPC measurement ($26.8/2 = 13.4 \text{ cm}^2/\text{Vs}$).

It is only possible to fit the experimental data by implementing an injection barrier (E_{barrier}), due to misalignment of the work functions of the contact and the conduction band of the perovskite, where the electron density at the contact (n_{contact}) is given as follows:

$$n_{\text{contact}} = N_c e^{E_{\text{barrier}}/k_B T}. \quad (5.3)$$

Then, at any given temperature, there will be a number of carriers that flow freely into the material to equilibrate the Fermi levels due to thermionic-emission-controlled injection. Without this barrier, the simulated current density is orders of magnitude larger than the experimentally measured current density. The device parameters for the room temperature fit are given in table 5.1 in chapter 2.3. It should be stressed here that, because the ion and trap density are within the same order of magnitude, the sharp onset expected for SCLC measurements is softened. This is explained in more detail in section 4.3.3 in chapter 4.¹¹

Additionally, the carrier density in the bulk of the MAPbBr₃ single crystal is simulated, as shown by the open circles in figure 5.6, and this is in good agreement with

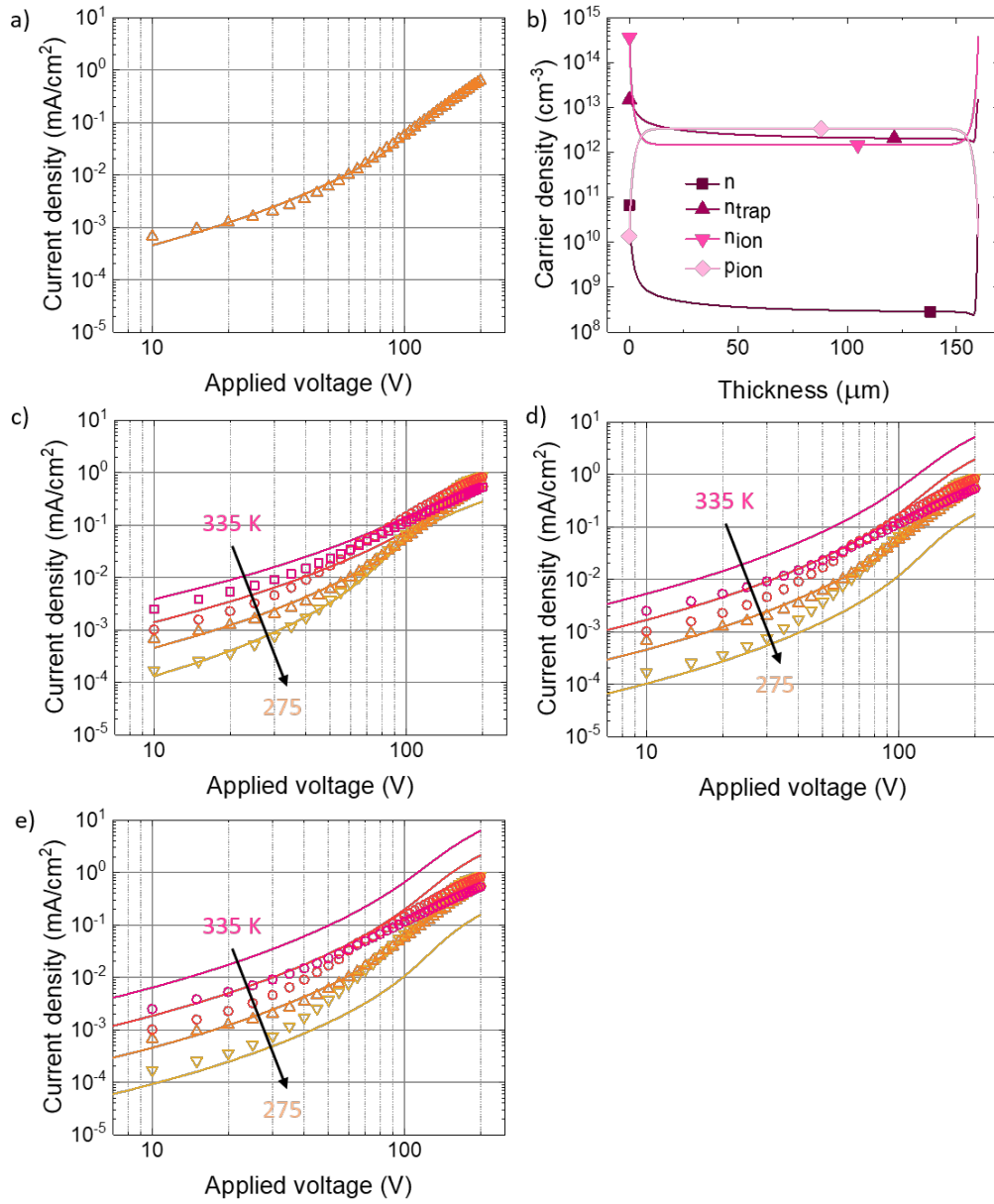


Figure 5.8: Simulations of the current-voltage characteristics (solid lines) of PV-SCLC measurements (scattered lines) of a 160 μm thick MAPbBr₃ single crystal. a) Fitting of the IV characteristics of PV-SCLC measurements at 295 K; b) Simulated free charge carrier density (n), trapped carrier density (n_{trap}) and ion densities (n_{ion} and p_{ions}) at 295 K in the low-voltage regime; c) Fitting of the IV characteristics of PV-SCLC measurements at 335 K, 315 K, 295 K and 275 K; d) Simulated IV characteristics at all temperatures where the injection barrier and the change in mobility govern the change in JV characteristics with temperature; e) Simulated IV characteristics at all temperatures where only the injection barrier between the electrode and the perovskite governs the change in JV characteristics with temperature. The simulations were performed in collaboration with Dr. V.M. Le Corre.

5.3. Results and Discussion

Table 5.2: Summarized extracted values from numerical modelling of the JV curve of 160- μm -thick MAPbBr₃ single crystal at room temperature.

Property	Value
Mobility	12.9 cm ² /Vs
Trap density	1.52 × 10 ¹³ cm ⁻³
Ion density	3.19 × 10 ¹² cm ⁻³
Carrier density	3.17 × 10 ⁸ cm ⁻³

the values extracted from fitting Ohm's law to region (1).

The extracted free carrier density and trap and ion densities as a function of position in the MAPbBr₃ crystal are reported in figure 5.8b, and the values in the middle of the crystal, as determined from room-temperature simulations, are summarised in table 5.2.

The fitted temperature-dependent JV characteristics are depicted in Figure 5.8c. To be able to fit the experimental data, several input parameters that change with temperature have to be accounted for. First, the mobility is varied with temperature, basing it on the measured room-temperature value and assuming the power law $\mu \propto T^{-1.5}$, which has been observed previously in other metal-halide perovskites, such as MAPbI₃.³⁵ Also, the density of states is varied as $N_C \propto T^{1.5}$ and the thermionic carrier injection following equation 5.3. Additionally, the soft nature of the perovskite material is taken into account, and therefore the trap density is varied with temperature via:

$$n_t = n_{t,0} e^{-E_{a,trap}/kT}, \quad (5.4)$$

where $n_{t,0}$ is the trap density value extracted from the numerical fit at room temperature, and $E_{a, trap}$ is the activation energy with which traps are induced as the temperature rises. The model also accounts for the equilibrium between free and trapped carriers, which varies with temperature. The ratio between ion and trap density is extracted at room temperature and, for simplicity, is kept constant at different temperatures, which appears to accurately reproduce the experimental

results. The assumption that is made here is that the ions and traps are related in some manner. As shown in figure 5.8c, there is good agreement between experimental and simulation data.

For a better understanding of the temperature-dependent fittings, some additional simulations were performed. Figure 5.8d shows that the conductivity increases with temperature in the low-voltage regime due to thermionic injection from the contact and thermal population from trapped carriers. This is simulated by letting both the injection barrier and mobility vary with temperature, while keeping the trap and ion density the same at all temperatures. The effect of reduced mobility with increasing temperature is strongly overshadowed by the thermal increase in carrier density. This is proven by simulating the JV curves when only the injection barrier is varied with temperature, but the mobility and ion and trap density is kept fixed at all temperatures, as shown in figure 5.8e.

Notably, the increase in trap and ion densities and decrease in mobility with increasing temperature influences the overall changes in conductivity with temperature in the opposite manner to the effect of increasing carrier density due to thermionic emission from the contact and the traps. With this study, it is emphasised that the fraction of free carriers in the system is governed by a combination of mechanisms that cannot be disentangled from each other via a single JV measurement. Therefore, it is stressed that, from dark-conductivity-extracted activation energies are *effective* activation energies ($E_{a, \text{eff}}$), and that these are mainly governed by the temperature-dependent density of traps and ions, temperature-dependent charge carrier mobility (both causing a decrease in conductivity with increasing temperature), and the injection barrier and ionization of trapped carriers (causing an increase in free-carrier density with increasing temperature). Overall, the model comprising these factors well describes temperature-dependent PV-SCLC data. Although some deviations can originate from the fact that it is assumed that the mobility varies with temperature as $\mu \propto$

$T^{-1.5}$, which is the case where the mobility is entirely governed by phonon scattering, scattering from defects may also be a contributing factor, which would lead to a slightly different temperature dependence.³⁵ Additionally, there may be a contribution to the thermal population of carriers from ionizable impurity donor or acceptor sites, which is not included in the model beyond the presence of ionizable traps. From the PV-SCLC measurements at different thicknesses, an average effective activation energy is calculated, which is independent of thickness, of (333 ± 26) meV for MAPbBr₃ and (217 ± 21) meV for MAPbI₃. The intrinsic conductivity increases more steeply with a lower band gap, and the extrinsic conductivity increases more steeply due to a lower barrier for thermionic emission, shallower traps, different temperature-dependent mobility, and different activation energy for trap generation.

5.4 Conclusion and Outlook

This chapter provides a detailed investigation into the changes in dark JV characteristics of metal-halide perovskite single crystals with changing temperature, and reveals electronic processes that affect the conductivity in these perovskite crystals. This is done via PV-SCLC measurements, which account for the presence of static ionic charge, but overcome the issue of having to deconvolute the influence of the movement of these ions, in combination with numerical modelling. Given the potential pitfalls of simple electronic characterisations methods such as SCLC measurements, it appears to be very reasonable to fit drift-diffusion simulations to the experimental data. Knowledge of the characteristic properties is of great importance for understanding the combined ionic and electronic conductivity in perovskites. Combining the findings reported here with other investigations on the influence of mobile ions, such as transient-ion-drift and impedance spectroscopy, will lead to a better understanding of the nature of the defects and the combined ionic and electronic properties of metal-halide perovskites and devices.

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**Understanding the Degradation of
Methylenediammonium and its Role in
Phase-stabilising Formamidinium Lead
Triiodide Single Crystals**

6.1 Context and Summary

Hybrid halide perovskites have huge potential for application in optoelectronic devices, and formamidinium lead triiodide (FAPbI₃) is seen as one of the most promising candidates to realise this. Despite its attractive low band gap, a key challenge for FAPbI₃ perovskite is to overcome its inherent ambient phase instability. Methylenediammonium dichloride (MDACl₂) has been used as an additive to repeatedly produce record efficiencies and enhance the stability of FAPbI₃. However, so far it has only been employed in polycrystalline films, where its exact role is uncertain. In this chapter, FAPbI₃ single crystals are grown from a solution containing MDACl₂ (FAPbI₃-M). It is demonstrated that FAPbI₃-M crystals are stable against transformation from the yellow perovskite phase (α -phase) to the black non-perovskite phase (δ -phase) for more than one year under ambient conditions, while FAPbI₃ crystals grown from a neat solution degrade within days. Critically, it is revealed by nuclear magnetic resonance (NMR) spectroscopy that the acidic MDACl₂ salt is unstable in solution and does not play an active role itself, but degrades instantaneously to produce ammonium (NH₄⁺) and methaniminium (meAn⁺). meAn⁺ subsequently oligomerises to yield hexamethylenetetramine (HMTA). FAPbI₃ crystals grown from a solution containing HMTA (FAPbI₃-H) replicate the enhanced α -phase stability of FAPbI₃-M. However, it is further determined that reaction of meAn⁺ with FA⁺ can interrupt HMTA cage construction, leading instead to tetrahydrotriazinium (THTZ-H⁺). In this chapter, it is postulated that THTZ-H⁺ is formed by the release of meAn⁺ from the dissolved crystals, and that meAn⁺ is the second cation responsible for increasing the phase stability of the FA-based lead halide perovskite.

6.2 Introduction

As discussed in chapter 2, hybrid organic-inorganic metal halide perovskites are recognized as one of the most promising emerging semiconducting materials for opto-

electronic applications due to their excellent properties including tuneable bandgaps,¹ high absorption coefficients² and long carrier diffusion lengths.³ Among the 'ABX₃' lead-halide perovskites reported to-date, FAPbI₃ has the narrowest achievable band gap,⁴ allowing for the highest theoretical photovoltaic power conversion efficiency (PCE) in a single-junction architecture,⁵ and contains the more thermally stable FA⁺ cation, replacing (MA⁺) employed in the archetypical early organic-inorganic perovskites. However, under ambient conditions, the cubic α -phase of FAPbI₃ (often referred to as the black phase) is thermodynamically unstable with respect to transformation to the non-perovskite hexagonal δ -phase (yellow phase), which possesses an undesirable wider band gap. Despite this, the phase transition is kinetically inhibited under ambient conditions permitting metastable α -FAPbI₃ to persist for hours, days and even months, with strong dependence on both conditions of processing and the relative humidity in which the processed material is stored.⁶ The phase stability of FAPbI₃ thin films and single crystals is necessary for their practical use, and major efforts are directed at finding approaches to suppress the α -to- δ phase transition. In particular, smaller A-site cations have been used to stabilise the perovskite lattice by alloying with FA. Most frequently used are MA⁺ (which reintroduced the thermal instability) and the alkali-metal Cs⁺,^{7,8} often in conjugation with I, Br and Cl X-site alloying. Despite such approaches being successful and creating stable and efficient wider-band gap perovskites, such as those required for tandem cells, they can introduce new challenges and undesirable properties. For instance, the increase in band gap due to structural changes induced by inclusion of smaller cations is not desirable for a single junction or middle junction in a triple junction cell.⁹ Furthermore, compositional inhomogeneities are often introduced, making the materials susceptible to cation segregation during water exposure and other impurity phase growths during aging.^{10,11}

Therefore, it is crucial to find strategies that improve the stability of FAPbI₃, without diminishing its material properties or compromising its thermal and ambient stability. Recently, much work has been focused on this challenge and most of the

latest single junction solar cell efficiency world record devices employ FAPbI₃ as the absorber layer.

In 2019, Min *et al.*,¹² reported highly efficient α -FAPbI₃ solar cells based on polycrystalline thin films by incorporating a small amount of methylenediammonium dichloride (MDACl₂, 3.8 mol% with respect to the Pb molarity) in solution, while maintaining the inherent band gap of FAPbI₃. They attribute the high certified PCE of 23.7% to the addition of MDACl₂. They report that MDA²⁺ leads to structural stabilisation of α -FAPbI₃ via partial replacement of FA⁺ with MDA²⁺ with additional interstitial Cl⁻ to compensate for the additional charge. In a subsequent work, Kim, *et al.*,¹³ propose that dual substitution of 0.03 mol% of Cs⁺ and MDA²⁺ on FA⁺ sites lowers the lattice strain and trap density in perovskite solar cells. In a third work – again from Seok and co-workers – MDA²⁺ was used alongside FAPbI₃ with a chemical bath deposited SnO₂ layer to reach the highest yet-reported efficiency of 25.8% (certified 25.5%) for perovskite solar cells.^{14,15}

In this chapter, as a means to simplify the system and understand the impact of additives upon material properties, we investigate single crystals of FAPbI₃ grown with different additives present. Here, the effect of adding MDACl₂ as an additive to the precursor solution during the growth of FAPbI₃ single crystals (referred to as FAPbI₃-M in the following) is studied. In a similar fashion to the previously reported polycrystalline thin films, here it is shown that crystals grown from this precursor solution possess vastly improved α -phase stability (> 1 year in air). Additionally, the crystals have significantly reduced defect density, as reflected in a greatly increased photoluminescence lifetime. To understand the impact of MDACl₂ on the growth of the single crystal, a detailed study of solution nuclear magnetic resonance (NMR) spectroscopy experiments of MDACl₂ is performed. It is found here that the highly acidic MDA²⁺ cation is not stable in solution and degrades immediately into several organic molecules, including hexamethylenetetramine (HMTA). The degradation is

further complicated by the presence of FA^+ in the precursor solution, where subsequent reactions with FA^+ can occur to form tetrahydro-1,3,5-triazinium (THTZ-H^+) as an alternative degradation product. By growing FAPbI_3 in the presence of HMTA, it is possible to replicate both the presence of THTZ-H^+ and the enhanced α -phase stability, and the proposed mechanism behind this is discussed in this chapter.

6.3 Results and Discussion

For this work, single crystal are grown via the inverse temperature crystallisation method, as discussed in chapter 3.^{16,17} The control FAPbI_3 single crystals are prepared by dissolving equimolar FAI and PbI_2 in GBL. Crystal growth is directed by addition of an appropriate seed crystal to this precursor solution. Heating to a temperature of 95 °C leads to growth of the seed into an α - FAPbI_3 single crystal between 2-4 mm in length. For the FAPbI_3 -M single crystals, 3.8 mol% is added (with respect to the Pb content) of MDACl_2 to the FAPbI_3 perovskite precursor solution. It is noted here that in contrast to Min *et al.* no MACl is added to any of the precursor solutions, since this work is aimed to isolate and investigate the effect of MDACl_2 on FAPbI_3 phase stability. To remove residual solvent, the crystals are heated in a vacuum oven at 180 °C for 30 minutes.

6.3.1 Electronic properties of FAPbI_3 single crystals

Here, the impact of MDACl_2 on the electronic properties of the FAPbI_3 single crystals using the PV-SCLC measurement, as introduced in chapter 4 is discussed. The JV characteristics are measured under vacuum and shown in figure 6.1a.¹⁸ The JV traces of both samples show an Ohmic region at low voltages. From this region the dark DC conductivity of $8.5 \times 10^{-6} \text{ Sm}^{-1}$ and $5.3 \times 10^{-6} \text{ Sm}^{-1}$ for FAPbI_3 and FAPbI_3 -M crystals, respectively are calculated. As derived in chapter 4, if the density of traps is larger than the density of static ionic space charge, the JV curve deviates from being

linear into a regime where the slope is larger than 2.^{18–20} From the voltage point at which this occurs, we can calculate a lower bound trap density (n_t) via:

$$n_t = \frac{2V_{\text{ons}}\epsilon_0\epsilon_r}{eL^2}, \quad (6.1)$$

where ϵ_0 is the vacuum permittivity, L the crystal thickness, e the electron charge and ϵ_r is the low frequency dielectric constant of the material, reported as 49.4 for FAPbI₃.²¹ Here, a similar value for ϵ_r is assumed for FAPbI₃-M. It is found here that the addition of MDACl₂ to the precursor solution reduces the trap density significantly from a lower-bound trap density of $1.1 \times 10^{12} \text{ cm}^{-3}$ for FAPbI₃ to $4.3 \times 10^{10} \text{ cm}^{-3}$ for FAPbI₃-M.

The improvement in optoelectronic quality of these FAPbI₃-M single crystals is supported by time-resolved photoluminescence (TRPL) measurements (depicted in figure 6.1b). Fitting of the TRPL decay traces reveals a significant increase in lifetime from 47 ns for the FAPbI₃ single crystal to 121 ns for the FAPbI₃-M single crystal at a fluence of 18 nJ/cm^2 .

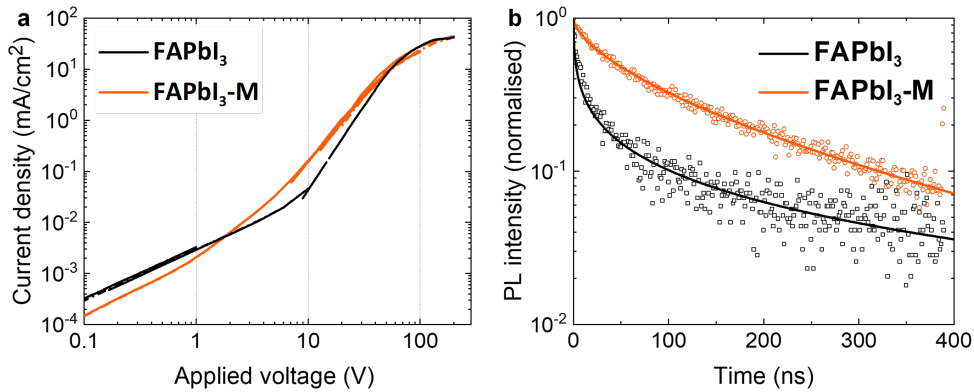


Figure 6.1: Electrical characterisation via space-charge limited current measurement of FAPbI₃ and FAPbI₃-M single crystals. a) PV-SCLC measurements for FAPbI₃ and FAPbI₃-M single crystals; b) time-resolved photoluminescence measurements of FAPbI₃ and FAPbI₃-M. The time-resolved photoluminescence measurements were performed by collaborator Dr. A. D. Wright.

The point of α -phase stability will be discussed later in this chapter, but here it is highlighted that the FAPbI₃-M crystals are significantly more stable under atmospheric

aging than the FAPbI₃ crystals. The results on electrical characterisation confirm that crystallising FAPbI₃ single crystals in the presence of MDACl₂ does result in improved optoelectronic properties and enhanced α -phase stability.

6.3.2 Degradation of MDACl₂

To understand how and why FAPbI₃ crystals grown in this manner have improved properties, a range of NMR spectroscopy techniques on solutions containing MDACl₂ are performed. As discussed above, it has been claimed previously that MDA²⁺ is incorporated within the cubic ABX₃ perovskite lattice on the A-site in solution-processed polycrystalline thin films based on FAPbI₃. This inclusion has been considered to be responsible for the enhanced α -phase stability. However, the presence of MDA²⁺ in any of our precursor solutions is not observed at any time. Instead, figure 6.2a shows the ¹H solution NMR spectra acquired from a solution of MDACl₂ dissolved in d⁶-DMSO at 1 minute, 10 minutes and 6 days after initial dissolution. It is apparent from figure 6.2a that the system evolves to contain just two ¹H signals. ¹H-¹H correlation spectroscopy (COSY) at the shortest time after dissolution, presented in figure 6.2b, reveals that these signals are uncoupled, and indeed their relative integrated ratios change over time, indicating the production of different species at different rates. The distinctive 1:1:1 triplet, initially at 7.30 ppm, migrates rapidly to 7.41 ppm after 10 minutes before stabilising, as is common for ammonium species under varying pH conditions. This signal is attributed to the presence of NH₄⁺ due to the coupling of ¹H nuclei with the quadrupolar $I = 1$ ¹⁴N nuclei.

Figure 6.2b also shows that the two other substantial signals in the ¹H solution NMR of the MDACl₂ solution after 1 minute correspond to nuclei present in the same species. This data, along with the concurrent formation of this species with ammonium and the chemical shifts of the signals, implicate methaniminium (meAn⁺,

figure 6.2c A) formation, as might be expected when MDA^{2+} is dissolved in pH neutral, aprotic polar solvents such as DMF, DMSO and GBL. The charge dense cation acts as a Bronsted acid before eliminating a secondary product, NH_4^+ to yield meAn^+ . This rapid release of acidic H^+ is the first step in an extended degradation sequence (figure 6.2c). Once produced, however, meAn^+ is itself unstable in solution, also acting as an acidic salt to transiently form methanimine (figure 6.2c B). Methanimine will rapidly oligomerise when present in sufficient concentrations. As set out in Step 2 of figure 6.2c, cyclisation to 1,3,5-triazinane (figure 6.2c C) followed by further additions of methaniminium and subsequent cage-closure, driven entropically by release of additional NH_4^+ , is expected to lead rapidly to the formation of HMTA-H^+ . Experimentally, between 1 and 10 minutes after initial dissolution of MDACl_2 a singlet signal of increasing intensity is observed in the ^1H solution NMR spectra at 4.83 ppm. By 6 days after initial dissolution the spectrum consists only of this singlet, the 1:1:1 triplet corresponding to ammonium and a broad singlet at 8.00 ppm. HMTA dissolved in $d^6\text{-DMSO}$ at neutral pH shows a singlet at 4.56 ppm. However, incremental addition of hydrochloric acid to this solution produces a downfield shift of this singlet to 4.83 ppm in line with the reported monoprotic pK_{aH} value for HMTA (4.93),²² confirming the identity of the final product of MDA^{2+} degradation as HMTA-H^+ . Integration of the relevant ^1H NMR signals confirms the stoichiometric 8:1 ratio of $\text{NH}_4^+:\text{HMTA-H}^+$ expected as a result of the proposed degradation route. The broad singlet at 8.00 ppm is attributed to the acidic ^1H of HMTA-H^+ . It should be emphasised here that despite the bias toward formation of HMTA-H^+ and NH_4^+ , all mechanistic steps are reversible and therefore it can be expected that the system at equilibrium will include small quantities of all intermediates.

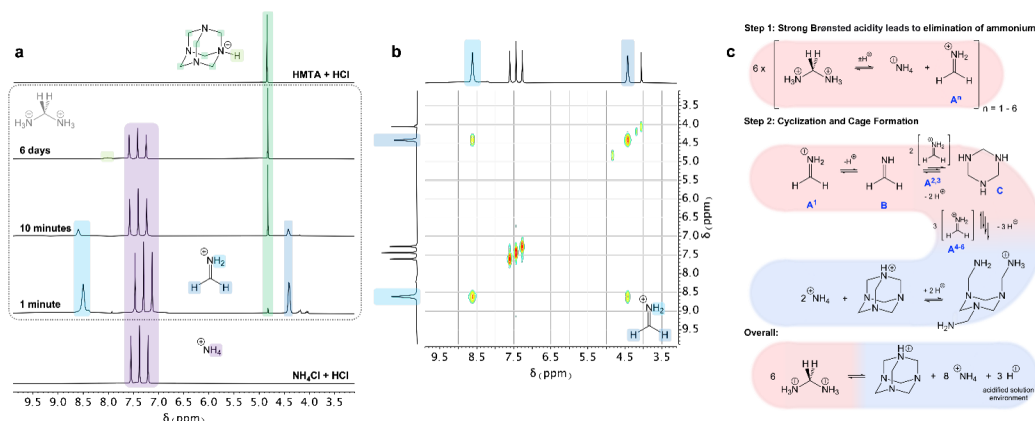


Figure 6.2: Degradation of MDA^{2+} a) ^1H solution Nuclear Magnetic Resonance (NMR) spectra tracking the evolution of MDACl_2 upon dissolution in d^6 -DMSO. Bottom: Spectra acquired from acidified solution of ammonium chloride, showing diagnostic 1:1:1 triplet. Variation in chemical shift of ammonium ^1H between samples is attributed to slight differences in pH. Top: Spectra acquired from acidified solution of (HMTA). Colour scheme correlates detected signals with ^1H chemical environments in detected species; b) ^1H - ^1H solution correlation spectrum of MDACl_2 degradation in-situ five minutes after initial dissolution in d^6 -DMSO; c) Degradation pathway of MDA^{2+} upon dissolution in a polar solvent. Hexamethylenetetramine (HMTA) and ammonia are represented in their protonated forms in line with our observations and on account of the acidic environment generated in solution as a result of the degradation. The NMR measurements were performed by collaborators B. Gallant and Dr. S. Collavini.

6.3.3 Single Crystal Phase Stability

Having identified HMTA as the degradation product of MDACl_2 , now it is investigated if it plays an active role in improving FAPbI_3 crystal properties. For this, HMTA is added during the crystal growth process and the α -phase stability of the as grown crystals when stored in ambient conditions is assessed. The additive is added at the stoichiometry expected in the case that 3.8 mol% MDACl_2 had degraded entirely to HMTA-H^+ (0.63 mol%).

The FAPbI_3 crystals grown in the presence of HMTA additive ($\text{FAPbI}_3\text{-H}$) show neither surface degradation, nor bulk degradation (figure 6.3a). For both FAPbI_3 and $\text{FAPbI}_3\text{-M}$ optically the growth of trace regions of a yellow phase on the crystal surface after only a few hours of storage in air are observed (figure 6.3a). However, for $\text{FAPbI}_3\text{-M}$ the degradation does not propagate significantly upon the surface, nor into the bulk of the material, as seen when the crystals are cleaved after 4 hours.

Initially the same is true for FAPbI₃ single crystals, although subsequent propagation of the yellow phase across the surface and into the bulk of the crystal does occur over the subsequent ten to hundreds of hours. Notably, the FAPbI₃-M crystals remain predominantly in their black α -phase after a year of storage.

To quantitatively track the phase stability of our crystals, we monitor the absolute Raman intensity of the best resolved δ -phase peak (at a Raman shift of 108 cm⁻¹) under ambient conditions (figure 6.3a). The peak intensity is proportional to the fraction of the probed surface layer that is in the δ -phase. The thickness of the probed layer for α -phase FAPbI₃ is estimated to be 100 nm via the absorption coefficient (ca. 1×10^5 cm⁻¹ at the Raman laser wavelength of 532 nm).²³ As shown in figure 6.3b, pristine FAPbI₃ undergoes detectable degradation after about 7 days, as indicated by the increase in intensity of the visible δ -phase peak. This signal detection shifts to 9 and 11 days for FAPbI₃-H and FAPbI₃-M, respectively. The rate of increase in δ -phase is around five times faster in FAPbI₃ than either FAPbI₃-M or FAPbI₃-H crystals. To demonstrate long-term stability, the measurements have been repeated on one-year-old FAPbI₃, FAPbI₃-M and 132-day-old FAPbI₃-H single crystals stored in vials, and 2500, 250 and 0 counts were detected, respectively.

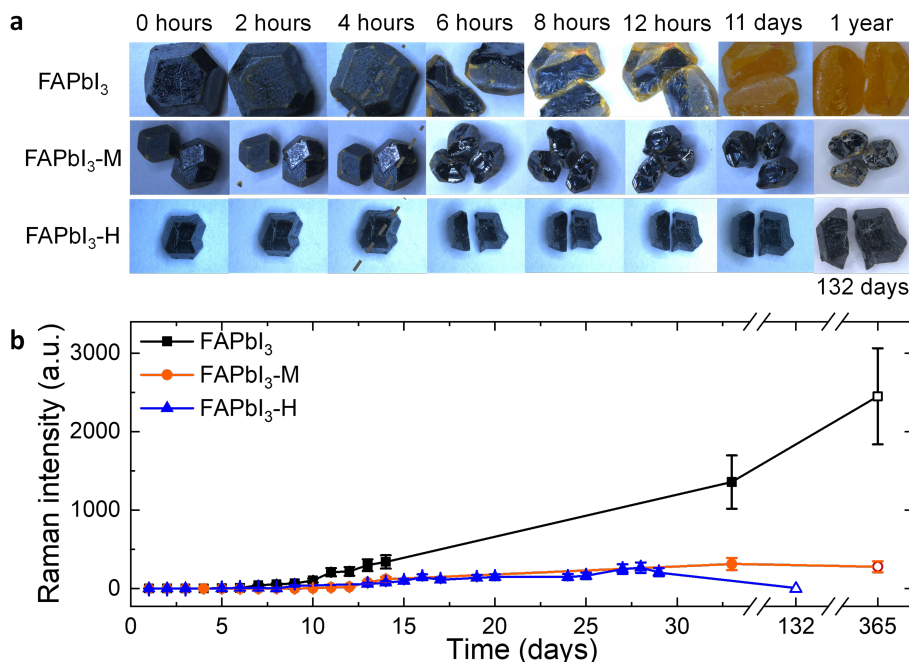


Figure 6.3: Single crystal stability upon ambient storage a) Optical microscope images of grown FAPbI₃, FAPbI₃-M, FAPbI₃-H crystals. The crystals are cleaved after 4 hours. The crystals were kept in glass vials under ambient conditions (dark, relative humidity 30-80%) throughout the measurement period; b) Temporal evolution of δ -phase Raman peak intensity for FAPbI₃, FAPbI₃-M, FAPbI₃-H single crystals. The single crystals were kept in air for the first 33 days and stored afterwards in a glass vial under ambient conditions. The Raman spectroscopy measurements were performed by collaborator B. Sturza.

Importantly, the onset in peak intensity for the δ -phase solely indicates a small fraction of the surface to be degraded. Cleaving FAPbI₃-H on day 29 and measuring the bulk of the crystal reveals a δ -phase intensity ratio bulk to surface of $I_{\text{bulk}}/I_{\text{surface}}(\text{HMTA}) = 0.14 \pm 0.05$. Repeating this on a separate FAPbI₃-M crystal after 285 days of aging gives a ratio of $I_{\text{bulk}}/I_{\text{surface}}(\text{MDA}) = 0.10 \pm 0.03$. This confirms that the observed δ -phase formation occurs in only a thin surface layer of the FAPbI₃-H and FAPbI₃-M crystals, while the bulk remains broadly unaffected. By contrast the pristine FAPbI₃ crystal is entirely converted to the δ -phase.

It is identified that HTMA plays a key role in the stabilisation of FAPbI₃-H crystals, but it is not yet established if this is due to its inclusion within the crystal, or

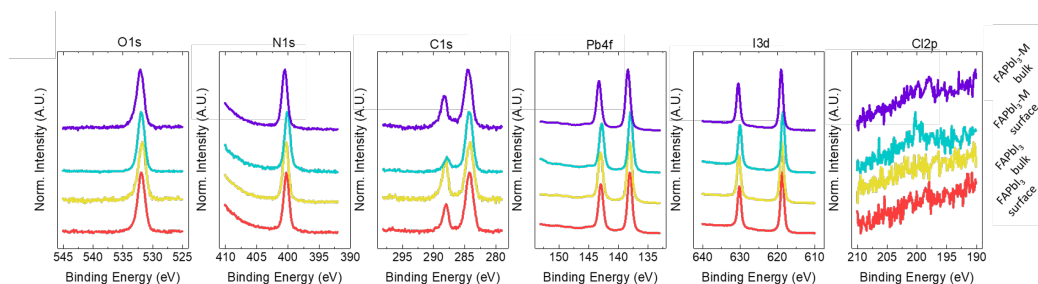


Figure 6.4: X-ray photoelectron spectroscopy (XPS) measurements on FAPbI₃ and FAPbI₃-M single crystals of O 1s, N 1s, C 1s, Pb 4f, I 3d and Cl 2p are performed to eliminate the possibility of chlorine incorporation in the single crystals. The XPS measurements were analysed in collaboration with Dr. A. Ramadan.

simply to its presence during crystallisation by influencing the FAPbI₃-H crystal quality.

To eliminate the possibility of these effects being due to incorporation of chloride (in the case of MDACl₂ addition), X-ray photoelectron spectroscopy (XPS) measurements are done on the single crystals, and presented in figure 6.4. No evidence of chloride is detected, and therefore it is excluded that chloride may be responsible.

6.3.4 Solution Chemistry of MDACl₂

Before further investigation on the presence of HMTA within the FAPbI₃ crystals, the solution chemistry of MDACl₂ in the presence of the perovskite precursor salts is further explored.

Acquisition of ¹H NMR spectra upon addition of 3.8 mol% MDACl₂ to separate solutions of FAI, PbI₂ and both in d⁶-DMSO reveal that the presence of the organic FA⁺ cation further complicates the degradation of MDA²⁺. Cage formation (step 2 in figure 6.2c) is interrupted by the addition of FA⁺, in place of further meAn⁺, during the oligomerisation of meAn⁺. Cyclisation with a single FA⁺ cation leads to THTZ-H⁺, an analogue of C in figure 6.2c.

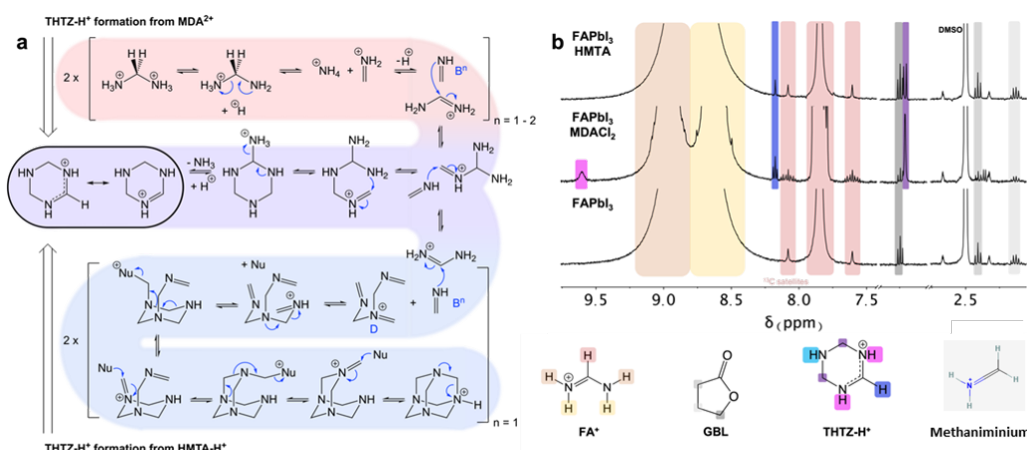


Figure 6.5: FAPbl₃ single crystal composition. a) Proposed mechanism for formation of THTZ-H⁺ from MDA²⁺ (top left) or HMTA-H⁺ (bottom right) via generation of two equivalents of methanimine, and reaction with FA⁺. Nu corresponds to any available nucleophile in solution, most likely HMTA additive; b) ¹H solution NMR spectra from the dissolution of FAPbl₃ grown in the presence of no additives (bottom), MDACl₂ (middle) and HMTA (top). The NMR measurements were performed by collaborators B. Gallant.

The formation of THTZ-H⁺ from MDA²⁺ or HMTA-H⁺ is accounted for mechanistically in figure 6.5a. The mechanism is proposed by collaborator B. Gallant. As all mechanistic steps are reversible, given a sufficient energetic or kinetic driving force methanimine formation can be achieved via the decomposition of either MDA²⁺ or of HMTA-H⁺ in a weakly acidic environment, in the presence of FA⁺.

To determine if any of the species observed during the degradation of MDACl₂ are incorporated, ¹H solution NMR on FAPbl₃ and FAPbl₃-M single crystals is conducted. As figure 6.5b shows, the presence of THTZ-H⁺ in FAPbl₃-M single crystals is observed, and there is no evidence for the presence of either HMTA or NH₄⁺. Considering that HMTA-H⁺ and NH₄⁺ are the dominant products of MDACl₂ degradation even in the presence of the FAPbl₃ precursors, this result is surprising.

Having established a causal link between the addition of HMTA – or species such as MDACl₂ which degrade into HMTA – to the crystal growth solution and both the enhanced phase stability of resultant crystals and the observation of THTZ-H⁺ in their ¹H NMR spectra, here a possible explanation for this link is discussed. Firstly,

as the cleaved α -FAPbI₃-M and α -FAPbI₃-H crystals, in which the bulk material is exposed to the same conditions as the surface, do not degrade at an enhanced rate (figure 6.3a) it is concluded that the source of stability improvements cannot stem from a surface effect alone and instead must originate in the bulk. To explain this bulk enhancement, it is proposed here that THTZ-H⁺ is formed only in solution upon dissolution of the crystals and that meAn⁺ is the organic cation incorporated in the growing FAPbI₃ single crystal on the perovskite A-site.

As has been discussed earlier, meAn⁺ is highly reactive in solution, oligomerising with methanimine to form HMTA-H⁺, and thus is present only transiently in the growth solution. However, were meAn⁺ incorporated into the solid state in a growing single crystal, it would be effectively isolated – in cationic form – from methanimine free in solution, and thus frozen out of further reactions. As noted above, the reversibility of all reaction pathways ensures small quantities of meAn⁺ are always present transiently in solution (when HMTA or MDACl₂ are present), even when the system reaches equilibrium. Incorporation of meAn⁺ into the perovskite lattice disturbs the system from equilibrium, resulting in replacement of meAn⁺ in solution. In this fashion a growing FAPbI₃-M or FAPbI₃-H single crystal could gradually incorporate substantial quantities of highly reactive meAn⁺.

6.4 Conclusion and Outlook

This chapter discusses how growth of α -FAPbI₃ single crystals in the presence of MDACl₂ leads to significantly reduced trap density and improved α -phase stability at room temperature, with FAPbI₃-M crystals remaining in the α -phase for more than a year. However, it is shown that MDACl₂ degrades rapidly in solution and so cannot be incorporated into the α -FAPbI₃ material. Via oligomerisation of methanimine,

6.4. Conclusion and Outlook

HMTA- H^+ and NH_4^+ are generated as majority degradation products. Despite α -FAPbI₃ crystals grown in the presence of HMTA demonstrating the enhanced α -phase stability, single crystals of α -FAPbI₃ grown in the presence of MDACl₂ or HMTA show no evidence of incorporation of either degradation products. ¹H solution NMR experiments show that in the presence of FA^+ , THTZ- H^+ can be formed as an alternative degradation product, which is stable in solution. Upon dissolution of FAPbI₃-M and FAPbI₃-H crystals in d⁶-DMSO, THTZ- H^+ is observed, however, THTZ is too large to be incorporated into the perovskite lattice. It is hypothesised that THTZ- H^+ is formed during the dissolution of the single crystals through small amounts of meAn^+ , which are incorporated into the single crystal. The symbiosis of both - meAn^+ and FAPbI₃ - to stabilise each other allows for a unique and previous unknown mechanism potentially revealing the existence of a new mixed-A-site lead-halide perovskite, namely $\text{meAn}_x\text{FA}_{1-x}\text{PbI}_3$. This perovskite is clearly capable of delivering high-efficiency PV cells with high α -phase stability.

Ongoing work on powder X-ray crystallography should be continued to index the space groups of FAPbI₃, FAPbI₃-M and FAPbI₃-H and precisely calculate their lattice parameters. Inclusion of meAn^+ at the A-site of the ABX₃ lattice is expected to reveal a contraction in the unit cell volume in both α -FAPbI₃-M and α -FAPbI₃-H in comparison to α -FAPbI₃.

Further work is required to both confirm this hypothesis, and to also assess if incorporation of this when-isolated-unstable-cation into the perovskite lattice, leads to long-term stable perovskite solar cells under the broad range of aging conditions that PV modules are exposed to during certification and under operation in the field.

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CHAPTER 7

Conclusion

Metal halide perovskites have become increasingly interesting for optoelectronic applications and photovoltaics. However, within contemporary sciences, such as perovskite device physics, often claims are made that exemplify remarkable properties of the materials used based on unsubstantiated methodologies. Therefore, the work in this thesis has predominantly focused on investigating the fundamental physics and improving the properties of hybrid metal-halide perovskite single crystals. The fundamentals required for this are outlined in chapter 2. Perovskite single crystals stand out as an ideal platform to study intrinsic properties of perovskites due to the absence of grain boundaries and enable thorough substantiated science on metal-halide perovskites. Additionally, they allow for the achievement of record-performance devices such as solar cells, photodetectors and ionization radiation detectors.

An often used method to measure properties of semiconductors is the space-charge limited current (SCLC) measurement, a technique that probes the extraction of current as a function of applied bias. Chapter 4 reveals how mobile ions can have a

dramatic effect on electronic current extraction during SCLC measurements, masking the underlying fundamental electronic properties of the semiconductor. To circumvent the effect of ions in electronic conductivity, a pulsed voltage SCLC (PV-SCLC) measurement methodology is introduced, which diminished the motion of mobile ions while measuring. With this new approach, electronic properties and trap characteristics can be accurately obtained from JV curves without hysteresis from semiconductors that exhibit both ionic and electronic conductivity.

Chapter 5 follows up on this with a detailed investigation into the temperature dependent changes in the dark JV characteristics of single crystals. Via the new PV-SCLC methodology that was introduced in chapter 4, in combination with numerical modelling described in chapter 2, electronic and ionic processes that affect the conductivity in perovskite crystals are revealed. The chapter shows that the background carrier density in perovskite single crystals is much higher than expected from thermally excited carriers from the valence band, and it highlights that different factors such as thermal injection from electrodes, trap and ion density, and temperature-dependent mobility can affect on the free-carrier concentration. Knowledge of these characteristic properties will be of great importance for understanding combined ionic and electronic conductivity in perovskites and for device optimization in perovskite applications.

The mixed ionic-electronic conductivity is one of the defining features of perovskite materials. While this can pose challenges to the electronic conductivity and intrinsic stability of light-emitting and photovoltaic devices as a result of accelerated ion migration during operations, going forward these properties are simultaneously interesting for alternative applications, such as rechargeable batteries and resistive switches for memory elements. Even though research on this is still at an early stage, the critical analysis of the effect of mobile ionic species on electronic conductivity represented in chapter 4 and chapter 5 can help to pave the way for realising the potential of hybrid perovskites in applications such as rechargeable batteries and in resistive switches for

neuromorphic computer systems. Especially in combination with other investigations on the influence of mobile ions, such as transient ion drift and impedance spectroscopy measurements, that can provide a better understanding of the nature of the defects and the ionic and electronic properties of perovskites.

Besides ionic motion, the perovskites technology also suffers from low stability and many researchers are focusing on improving device stability. Generally, thin film based perovskite solar cells have high defect density and many grain boundaries. Defects and grain boundaries often are responsible for low stability towards humidity and temperature, and can act as recombination centres that accelerate degradation. Generally, perovskite single crystals have much better stability due to fewer defects and absence of grain boundaries. However, FAPbI₃, which has the lowest achievable band gap of lead-based perovskites, and therefore allows for the highest theoretical photovoltaic power conversion efficiency, is thermodynamically unstable with respect to transformation to the non-perovskite yellow phase with undesirable wider band gap. Therefore, chapter 6 focuses on the use of additives to the precursor solution of FAPbI₃ single crystals.

Growth of α -FAPbI₃ single crystals in the presence of MDACl₂ additive leads to significantly reduced trap density and improved α -phase stability at room temperature, with FAPbI₃-M crystals remaining in the α -phase for more than a year. It is, however, shown that MDACl₂ degrades rapidly in solution and so cannot be incorporated into the α -FAPbI₃ material. MDACl₂ produces ammonium (NH₄⁺) and methaniminium (meAn⁺). meAn⁺ subsequently oligomerises to yield hexamethylenetetramine (HMTA).

Despite α -FAPbI₃ crystals grown in the presence of HMTA demonstrating the enhanced α -phase stability, single crystals of α -FAPbI₃ grown in the presence of MDACl₂ or HMTA show no evidence of incorporation of either degradation products.

It was detected that in the presence of FA^+ in the precursor solution, multiple subsequent reactions with FA^+ can occur. One of the degradation products being THTZ-H^+ , which is stable in solution. However, THTZ is too large to be incorporated into the perovskite lattice. It is hypothesised here that THTZ-H^+ is formed during the dissolution of the single crystals through small amounts of meAn^+ , which are incorporated into the single crystal. The symbiosis of both, meAn and FAPbI_3 , to stabilise each other allows for a unique and unrepresented mechanism and potentially reveals the existence of a new mixed-A-site lead-halide perovskite, namely $\text{meAn}_x\text{FA}_{1-x}\text{PbI}_3$. This perovskite is clearly capable of delivering high-efficiency PV cells with high α -phase stability. Further work is required to confirm this hypothesis, and to assess if incorporation of this when-isolated-unstable-cation into the perovskite lattice, leads to long-term stable perovskite solar cells under the broad range of aging conditions that PV modules are exposed to during certification and under operation in the field.

As we stand, material characterization techniques are being applied liberally within the field of perovskite photovoltaics to extract key 'figures of merits' on electrical characterization, material properties and stability. The work in this thesis emphasises that it is of great importance that experimental conditions and analysis routines are clearly described and carefully conducted in order to accurately interpret perovskite-based device measurements, and achieve comparability between different laboratories. More accurate measurements on the fundamental properties of perovskites should ultimately lead to more effective development of their applications.

APPENDIX A

Appendices

Table A.1: Summary of device dimensions and respective extracted properties.

Crystal	t (μm)	A (cm^2)	σ (S/m)	μ (cm^2/Vs)	n (cm^{-3})	N_d (cm^{-3})	N_c (cm^{-3})	E_a (eV)	E_t (eV)
MAPbBr ₃	160	0.114	1.02×10^{-7}	26.8	2.37×10^8	5.86×10^{10}	2.77×10^{18}	0.136 ± 0.008	0.066 ± 0.016
MAPbBr ₃	210	0.121	6.42×10^{-8}	26.8	1.50×10^8	5.86×10^{10}	2.77×10^{18}	0.135 ± 0.009	n.a.
MAPbBr ₃	335	0.139	7.68×10^{-8}	26.8	1.79×10^8	5.86×10^{10}	2.77×10^{18}	0.116 ± 0.009	n.a.
MAPbI ₃	240	0.042	2.04×10^{-7}	44.6	2.86×10^8	9.75×10^9	2.32×10^{18}	0.085 ± 0.011	0.072 ± 0.006
MAPbI ₃	280	0.057	4.43×10^{-7}	44.6	6.20×10^8	9.75×10^9	2.32×10^{18}	0.070 ± 0.005	0.100 ± 0.008
MAPbI ₃	290	0.093	4.39×10^{-7}	44.6	6.15×10^8	9.75×10^9	0.085 ± 0.013	0.089 ± 0.008	

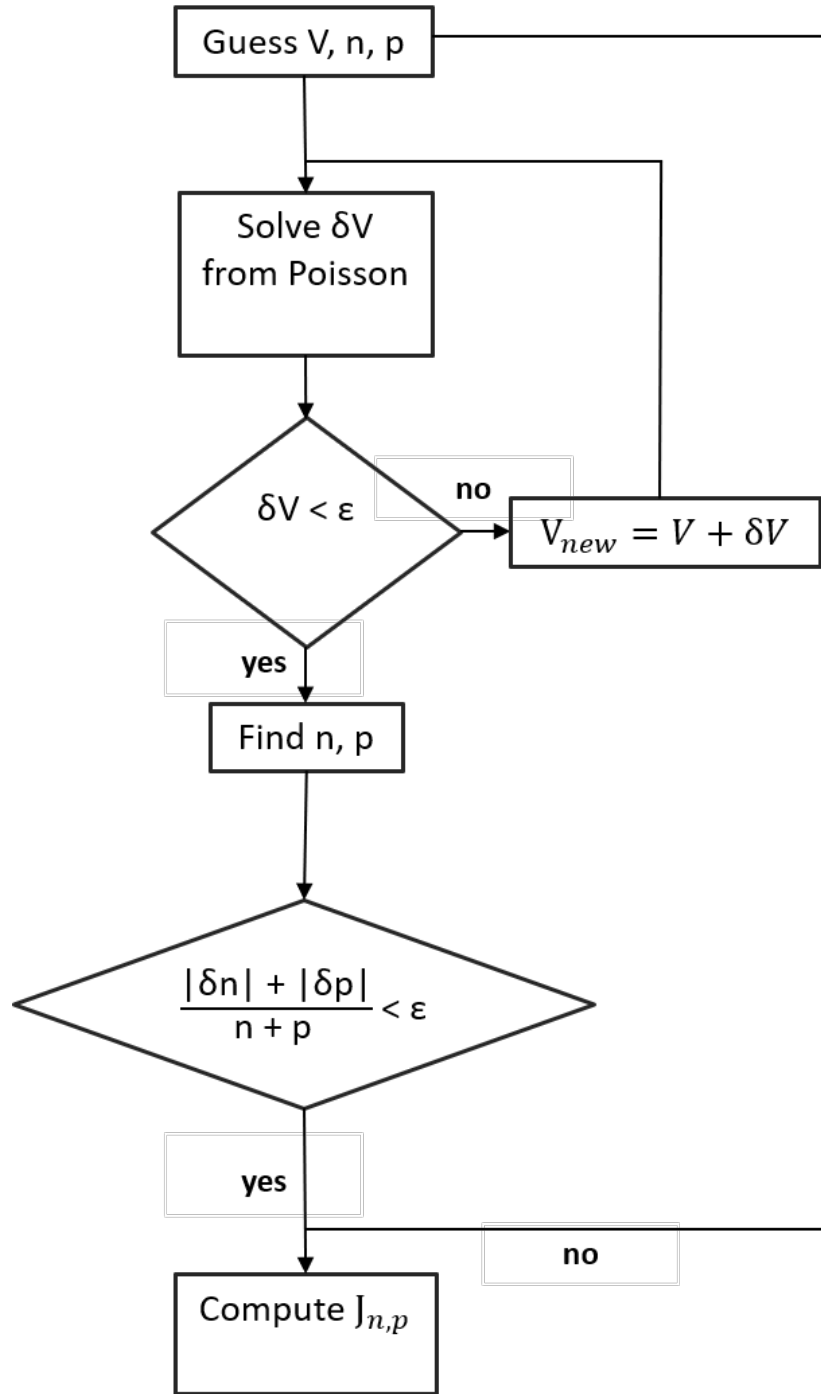


Figure A.1: Flow diagram of the simulation program. To solve the basic equations, Gummel iteration is used. First a guess is made for the potential and electron and hole charge carrier densities. Then, a correction (δ) to the guessed potential is calculated from Poisson's equation. This correction is added to the guessed potential and this process is repeated until convergence is reached. Next, the charge carrier densities are calculated from the new potential by solving the continuity equations. The full procedure is repeated until the change in the carrier densities becomes very small, i.e., until convergence is reached.¹

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