Photophysics of Metal Halide Perovskites

Tekelenburg, Eelco Kinsa

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Chapter 1

Introduction

Attitudes to global warming have transitioned from being a scientific curiosity to an acknowledged fact of life that requires action from all parts of society. The Net Zero Emissions by 2050 Scenario aims to keep the average global temperature rise to 1.5 °C. Although renewable energy records continue to be set, meeting this target necessitates renewable electricity to grow twice as fast from 2022 to 2030 compared to the average expansion from 2019 to 2021.[1] For solar photovoltaics (PV), the third largest renewable electricity generator, the annual growth in generation must triple to stay in line with the Net Zero Emissions Scenario.[2] These numbers illustrate that an increased effort is required from both public and private stakeholders to advance the role of solar PV. This thesis contributes to this need by exploring a semiconducting material class known as metal halide perovskites that show great promise in solar cells.

The story of solar cells started in 1839 when Alexandre-Edmond Becquerel observed the photovoltaic effect in electrolyte solutions, although he could not explain the effect.[3] It was much later, in 1883, that Charles Fritts made the first solar cells from selenium. However, the low efficiencies below 1% inhibited practical use. The foundations of the first practical solar cell were laid in the 1940s by Russell Shoemaker Ohl who made a p-n junction, which lead to the first practical silicon solar cell with about 6% efficiency announced by Bell Labs in April 1954.[3] The record for a silicon research cell has now reached 27.6% through continuous development and innovations.[4] The success of solar PV can also be measured by the price of the electricity generated as it is becoming the lowest-cost option.[2] It is this first generation of silicon solar cells that are predominantly seen on rooftops and in utility-scale solar farms. It is foreseen that silicon will remain dominant in the solar PV market in the near future, considering that in 2021 95% of the production of solar PV was based on crystalline silicon wafers.[5]

However, crystalline silicon has the inherent disadvantage of being an indirect semiconductor such that thick layers are needed for efficient solar cells. This results in heavy and non-transparent solar cell modules that impose limitations on their applications. Thin film solar cells are also being developed, based on direct band gap semiconductors such as CdTe or CIGS, allowing lightweight applications such as placement on warehouse rooftops. In recent years, the efficiency of these so-called second-generation solar cells has steadily improved to 22%.[4] However, their market share has remained small.

It is for a steep rise in power conversion efficiency - from 3.8% at their discovery in

2009 to 25.8% in 2022 - that solar cells based on metal halide perovskites have attracted significant attention.[6],[4] This emerging PV technology has the potential to realise new applications in areas such as building-integrated PV, automotive, and the Internet of Things (IoT).[7] This promise has spurred over 20 companies worldwide to bring perovskites to the market.[8] Metal halide perovskites can be made flexible, semitransparent, and deposited on a large scale.[7] Besides solar cells, metal halide perovskites can be applied in light-emitting diodes (LEDs),[9] photodetectors,[10] and lasers.[11] However, many challenges remain before commercialisation becomes viable, and much of the fundamental physics is not fully understood.

One of the challenges for commercialisation is the low stability of metal halide perovskites, which are sensitive to moisture, oxygen, light, and temperature - factors that are intrinsically related to the crystal structure.[12] The incorporation of large organic cations in the structure has been shown to improve the thermodynamic stability of the semiconductor material as structures with reduced dimensionality are then formed.[13] This topic was extensively investigated in the 1990s and early 2000s, and renewed interest has emerged in the last 5 to 10 years. The chemical and structural freedom of these low-dimensional structures allows for fine-tuning of their optical and transport properties.[14] Thus, a rich and exciting research field has developed, where many questions remain to be answered.

The high-efficiency solar cells mentioned above use perovskites containing lead (Pb). Although the use of Pb falls within current heavy metal regulations in electronics, there is growing concern about the toxicity of Pb and its environmental impact.[15] Replacing Pb with the less toxic tin (Sn) allows many of the most desirable properties to be maintained such as a high absorption coefficient and an ideal band gap to reach power conversion efficiencies above 30%.[16] Further attractive properties such as long-lived hot carriers have been demonstrated, potentially enabling solar cell efficiencies beyond the detailed balance limit of 33%.[17] However, Sn-based perovskites are notoriously unstable and have fast crystallisation dynamics, making them challenging to work with.[16] This has been reflected in the solar cell efficiency which remained around 6% for many years. A breakthrough to 9% was realised in our group in 2018; since then their efficiencies have reached over 14% but fundamental questions remain to be answered.[18],[19] This thesis aims to improve the understanding of the photophysics of a wide range of perovskite compositions in order to provide a foundation and guidance for future work.

Outline of this thesis

In Chapter 2 the theoretical background is provided, needed as a foundation for the research presented in Chapters 3 to 7. We start by discussing the 3D perovskite crystal structure and electronic band structure. Next, we focus on lower-dimensional structures and their optical properties. Finally, we introduce the basics of hot-carrier dynamics to understand the key properties that might enable solar cells beyond 33% efficiency.

Although the optical properties of low-dimensional perovskites have been reported since the early 90s,[20] the renewed recent interest in these materials has resulted in optical phenomena that have been subject to discussion. Chapter 3 discusses the broad photolu-

minescence features encountered in two low-dimensional perovskite crystals: $(PEA)_2PbI_4$ and $(FPEA)_2PbI_4$. We show that the origin of the broad emission is related to defects and can be proven by an elegant below-gap excitation experiment, hereby resolving the debate about its origin in the scientific literature.

In Chapter 4 we continue the investigation of Chapter 3 by looking at the narrow photoluminescence feature of the same compounds. We report high-resolution measurements at liquid helium temperature that reveal previously unknown features. Interestingly, these materials have strong exciton-phonon coupling that causes emission on the high-energy side of the spectrum, whereby the choice of the organic spacers determines the energy separation of the peaks. By varying the temperature, we could identify emission peaks from bound excitonic states on the low-energy side, highlighting the complexity of the photoluminescence spectra.

The perovskite field has focused thus far mainly on Pb-based perovskites, such that a gap exists in the knowledge of Sn compounds. In Chapter 5 two new Sn-based single crystals are reported that differ in their structural connectivity: a planar $\langle 100 \rangle$-oriented and a corrugated $\langle 110 \rangle$-oriented perovskite, where the choice of the diammonium cation templates the desired structure. The structural differences result in entirely different emission bands and concomitant physics, as revealed by temperature-dependent photoluminescence spectroscopy. Intriguingly, we also show that thin films of one of the compounds can be obtained in two different crystalline phases by changing the annealing temperature from 70 °C to 100 °C.

Slow cooling of hot carriers could allow for solar cell efficiencies to reach beyond 33%, and several studies have reported on slow cooling in metal halide perovskites. However, there is currently no consensus on the mechanism involved and the impact of the small cation on the cooling dynamics. The last two chapters of this thesis are devoted to unravelling this issue by studying a series of Sn-based perovskites. In Chapter 6 we optimise the deposition parameters to obtain high-quality thin films of tin iodide perovskites containing the three most common small cations: methylammonium (MA), formamidinium (FA), and caesium (Cs). At room temperature, we show that these hybrid organic-inorganic perovskites exhibit hot-carrier cooling dynamics up to 6 ns, while the inorganic Cs perovskite is completely cooled on a sub-nanosecond timescale. The result is a larger hot-carrier contribution to the photoluminescence of the hybrid compounds compared to the inorganic compound.

A deeper investigation of these compounds is presented in Chapter 7. At a temperature of 4.4 K, both $CsSnI_3$ and $FASnI_3$ have a similar magnitude of the hot-carrier photoluminescence, which is the result of filling of the electronic band edge. On the other hand, the cation has a large impact on the vibrational structure with a faster phonon decay for the hybrid compound. These results not only explain the hot-carrier dynamics in perovskites but also give insight into new design principles for the discovery of unexplored hot-carrier materials.

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