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Metal Halide Perovskites

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Metal Halide Perovskites

Composition, Physical Properties and Applications

Bart Groeneveld

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Composition, Physical Properties and Applications

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CHAPTER 1

Introduction

Materials and societal development have been closely intertwined throughout the history of mankind. The important role that materials played in the evolution of civilizations is reflected in the names of three historic time periods: the Stone Age, Bronze Age and Iron Age — all of which pay tribute to the material that helped to propel technological advances during that time. In all of these periods the discovery of new materials opened up possibilities to develop more modern tools and technology which could improve the quality of human life. However, it is also possible for this synergy to work the other way around, where technology calls for the development of novel materials with specific properties. The latter option has become very important in the twentieth century, leading to the growth of the field of advanced materials.

The rise of (nano)technology made it possible to develop new materials which are engineered to have superior properties compared to conventional materials.^[1] These improved materials are also referred to as advanced materials. An interesting class of advanced materials are the inorganic-organic hybrids. These combine the advantages of inorganic materials, such as bandgap tunability and high electrical mobility with those of organic materials (ease of processing, versatility in functionalization) into a new, hybrid structure.^{[2],[3]} Examples of hybrids are metal-organic frameworks,^[4] colloidal inorganic nanoparticles capped with organic ligands,^[5] polymer-wrapped single-walled carbon nanotubes,^[6] and hybrid inorganic-organic perovskites.^[2] The last class is very broad and has been studied for decades.^[7] The ability to design perovskites — by changing the elements that make up the material (see Section 1.1) — enables their use in many optoelectronic applications, such as in the fabrication of photodetectors, lasers and light emitting diodes.^{[8]–[10]} However, their main use in optoelectronics is in thin film solar cells^{[11]–[14]} and this will be addressed in Section 1.2.1.

Figure 1.1: The ABX_3 perovskite crystal structure.

Outside the realm of optoelectronics, hybrid perovskites have been used to make sensors to detect gases or vapors (Section 1.2.2).^{[15],[16]} This seemingly broad range of applications has one common denominator: it is based on the metal halide perovskites, a subset of the hybrid perovskites. This thesis focuses on studying this class of materials, which is described in more detail in Section 1.1.

1.1 Metal halide perovskites

The perovskite crystal structure can be described by the ABX_3 formula.^[17] In the case of metal halide perovskites A is a monovalent cation, B a divalent cation and X a monovalent anion. This crystal structure is depicted in Figure 1.1 and can be described as a network of corner-sharing BX_6 octahedra with the A cations situated in the middle between eight octahedra. The B site is occupied by a metal ion and the halide ions are located on the X positions. The unit cell is completed by a cation at the A site, which can be either organic or inorganic. Depending on the radii of the ions involved, the perovskite structure can be cubic or pseudocubic. This can be predicted by the Goldschmidt tolerance factor t :

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}, \quad (1.1)$$

where r_A , r_B and r_X are the ionic radii of A, B and X, respectively.^[17] A tolerance factor between 0.9 and 1 will lead to a cubic perovskite structure, and the structure will be a distorted perovskite for t between 0.8 and 0.89, due to the tilting of the octahedra. For t below 0.8 and higher than 1, there is a mismatch between the sizes of the ions and the structure will not form a perovskite.^[18] Any combination of ions that matches both criteria (obeying the charge distribution for the ions and having a suitable value for t) could form a perovskite. This means that there is a large number of perovskites that could be synthesized by picking the right elements.^{[19],[20]}

Compared to oxide-based perovskites (where X is not a halide but an oxygen ion instead), metal halide perovskites are obtained at much lower temperatures due to the fact that they can be deposited from solution.^{[21]–[23]} In fact, the solution processing can often take place at room temperature (after which annealing at temperatures around 100°C might be necessary). This is one of the key strengths of metal halide perovskites, as it allows for easy fabrication. Synthesizing a new metal halide perovskite can therefore be very straightforward: changing the precursor salts in the solution will often suffice — as long as the intended compound follows the two criteria described above. Another advantage of the solution processability is that these hybrid inorganic-organic metal halide perovskites can be obtained in a crystalline form, which is not typical for inorganic-organic hybrids.^[23] Single crystal metal halide perovskites were used for this thesis, specifically for Chapters 3 and 4. However, the majority of the research was conducted on thin film samples. These typically have a thickness on the order of 10^1 - 10^3 nm and are fabricated by techniques such as spin coating and blade coating. Thin film samples were studied in all Chapters of this thesis. The aforementioned solution processing techniques are very versatile and can be used to produce perovskite films with the dimensionality of one's choice, such as three- and two-dimensional metal halide perovskites. The role of the dimensionality of the metal halide perovskite in determining its properties will be addressed in the following two sections, starting with the three-dimensional case.

1.1.1 Three-dimensional metal halide perovskites

When the term perovskite is used without any additional information, it is usually assumed that the material in question is three-dimensional. The dimensionality of the perovskite refers to the crystal structure. The ABX_3 formula describes the unit cell, which forms a three-dimensional perovskite if there are no constraints for the number of repeat units in the x, y and z direction on a nanoscopic scale. As a consequence, quantum confinement effects play no role in three-dimensional perovskites, unlike in lower-dimensional ones.

The most commonly studied 3D metal halide perovskite is methylammonium lead triiodide ($CH_3NH_3PbI_3$, also referred to as methylammonium lead iodide, or $MAPbI_3$). This material, which has been studied for its use in solar cells since 2009,^[11] was used in Chapter 2. $MAPbI_3$ is used in various other optoelectronic devices, such as photodetectors, light emitting diodes, and lasers.^{[8]–[10],[24]–[26]} The use of three-dimensional lead halide perovskites for these applications is a result of their advantageous properties.

A very important property of metal halide perovskites is the fact that their bandgap can be tuned. Tuning is achieved by changing the elements in the perovskite structure, keeping the Goldschmidt tolerance factor (Equation 1.1) in mind. Methylammonium lead iodide has a bandgap of 1.55 eV, whereas substituting bromide for iodide results in a bandgap of 2.3 eV for methylammonium lead tribromide ($MAPbBr_3$). This higher bandgap results from a

1.1. METAL HALIDE PEROVSKITES

combination of a lower valence band maximum (VBM) and a higher conduction band minimum (CBM). The VBM consists of anti-bonding Pb-*s* and X-*p* orbitals,^{[27],[28]} and the latter are lowered when a smaller halogen ion is involved due to the higher electronegativity.^[28] As a result, the VBM shifts downward for smaller halides, increasing the bandgap. Additionally, the CBM, consisting of anti-bonding Pb-*p* and X-*s* orbitals^[27] — albeit of more ionic character than the VBM, with the Pb orbitals contributing about 70-90%^[29] —, shifts upward when going from I to Br to Cl.^[28] This is mainly caused by the shift in the Pb-*p* atomic level, which Tao et al. attributed to a stronger confinement effect for Pb as the Pb-X distance decreases.^[28]

In addition to changing the halide ions in the MAPbX₃ structure, one can also replace the A-site cation by other organic cations (such as formamidinium (H₂N-CH=NH₂⁺, abbreviated as FA), or by elements such as cesium.^{[30]–[32]} The commonly used organic cations are depicted in Figure 1.2. Substituting the organic cation leads to a change in bandgap from 1.55 eV for MAPbI₃ to 1.48 eV for FAPbI₃. For the purely inorganic CsPbI₃, this effect is even more pronounced: its bandgap is 1.73 eV.^[31] Interestingly, this effect is not the result of a direct influence of the cation on the position of the VBM and CBM, since the associated energy levels are located far from these regions.^{[28],[33]} Instead, the cation plays a role by influencing the overlap of the Pb-*s* and X-*p* orbitals in the VBM. This can be the result of a change in size of the lattice and of the tilting of the PbX₆ octahedra — i.e. when the Pb-X-Pb angles are not 180° (see Figure 1.3) — and the effect is dependent on the symmetry of the material.^[29] More Pb-X overlap results in a higher energy for the anti-bonding orbital, hence a smaller bandgap.^{[29],[34]} In a cubic system, the tilting is not present and therefore, the size of the cation will determine the Pb-X overlap: the smaller the cation, the more Pb-X overlap.

In a non-cubic system, tilting of the octahedra will decrease the Pb-X overlap. Meloni et al. found that the effect of tilting often dominates in non-cubic perovskites, thereby reducing the overlap in materials with a smaller cation.^[29] For the examples of cations given before (MA, FA, Cs), this can be rationalized as follows. FAPbI₃ belongs to the trigonal $P\bar{3}m1$ space group, which is close to the cubic $Pm\bar{3}m$ space group.^[35] MAPbI₃ belongs to the tetragonal $I4/mcm$ space group, and displays octahedral tilting.^{[36],[37]} The tilting leads to a higher bandgap for MAPbI₃, despite the smaller size of the MA ion compared to FA. The ionic radius of cesium is considerably smaller than both MA and FA: 1.81 Å versus 2.70 Å and 2.79 Å, respectively (as determined by density functional theory calculations).^[35] Based on the size of the cation alone, one would expect a lower bandgap for CsPbI₃ than for MAPbI₃. However, in this case, the crystal symmetry is the cause behind the difference in bandgap between CsPbI₃ and the MA-equivalent. The room-temperature perovskite phase of CsPbI₃ belongs to the orthorhombic $Pnam$ space group, and shows significant octahedral tilting.^[38] The orthorhombic polymorph of MAPbI₃, which occurs at temperatures below

Figure 1.2: Molecular structures of methylammonium and formamidinium.

Figure 1.3: An example of octahedral tilting in perovskites. In this case the tilt (with angle θ) is out-of-phase ($a^0a^0c^-$ in Glazer notation).^[40] Tilting can occur along every direction in perovskites, and can also be of the in-phase type.^[41]

170 K, has a bandgap which is around 110 meV higher than the tetragonal room-temperature phase.^{[38],[39]} Sutton et al. noted that this value is very similar to the 170 meV difference in bandgap between orthorhombic CsPbI_3 and tetragonal MAPbI_3 , and attributed the large difference in bandgap to the change in crystal structure.^[38]

The bandgap is not the only property of the metal halide perovskite that changes upon elemental substitution. For example, humidity causes MAPbI_3 to degrade. Additionally, the stability of MAPbI_3 under solar illumination in dry air is low. When iodide is replaced by bromide, the stability increases significantly.^[42] However, this material is less suitable for solar cell applications due to its wider bandgap — the ideal value of the bandgap for highest potential efficiency in a single junction solar cell is 1.34 eV.^[43] FAPbI_3 , with a bandgap of 1.48 eV, is closer to the optimum. The downside is that this material is also very unstable in humid atmosphere.^[44] It seems that one would need to combine the advantageous properties of various elements in order to produce a stable perovskite with a suitable bandgap, which

is a topic that will be addressed later.

Another relevant aspect of the stability of metal halide perovskites is related to ion migration. Theoretical work on the formation energy of defects in MAPbI₃ indicates that iodide interstitials and vacancies of methylammonium, lead and iodide are formed easily.^{[45]–[47]} After taking the diffusion barrier into consideration, it was found that iodide vacancies have the lowest energetic barrier to diffuse;^{[46],[48]} this migration was confirmed experimentally.^{[49],[50]} The ion migration is affected by electrical bias and illumination — in the latter case the activation energy of the defect is reduced significantly.^{[50],[51]} In solar cells this effect can lead to a number of problems, such as hysteresis (see Section 1.2.1). The migration of iodide can also degrade the solar cells if the ions leave the perovskite layer. For instance, iodide was found to react with the silver electrodes of perovskite solar cells,^{[52],[53]} or affect other layers in the devices.^[54]

So far, we have discussed metal halide perovskites with only one element for each position in the ABX₃ framework. However, it is possible to mix the elements, keeping the Goldschmidt tolerance factor in mind. Examples of this in literature are MAPbI_{3-x}Br_x — for which x can be varied from 0 to 3 —^{[55],[56]} (FAPbI₃)_{1-x}(MAPbBr₃)_x^[57] — x from 0 to 1 —, and FA_{0.83}Cs_{0.17}PbI_{1.8}Br_{1.2}^[58]. Though an important motivation for mixing elements is to improve the stability of the material, mixing can also enable phase segregation. For instance, in mixed iodide-bromide perovskites, photoexcitation can cause halide segregation. It was found that light-induced segregation leads to iodide-rich regions, and the effect is reversible: these regions disappear after the perovskite is kept in the dark.^{[59],[60]} Therefore, the properties of the mixed perovskite are highly dependent on the stoichiometry. In Chapter 3, our work on Cs_{0.1}FA_{0.9}PbI_{3-x}Br_x is presented, in which we show that small changes in stoichiometry can have a big influence on phase purity. The aforementioned mixed perovskites typically have a higher structural stability than MAPbI₃ and FAPbI₃, combined with a bandgap suitable for photovoltaic application.^{[58],[61]–[63]}

The ability to tune the bandgap of metal halide perovskites is not the only reason why this class of materials has been used intensively in photovoltaics and other optoelectronic devices. Three-dimensional lead halide perovskites are also known for their high absorption coefficient. This is a result of the direct p - p transition in these materials. The lower part of the conduction band of MAPbI₃ is largely composed of Pb- p orbitals. The dispersion for these orbitals is lower than for s bands. As a result, the density of states at the edge of the conduction band is higher than for semiconductors with a dispersive s -band at the bottom of the conduction band, such as GaAs. The higher density of states leads to a stronger optical absorption.^[64] This makes it possible to use perovskite films with submicron thickness for photovoltaic application.

Upon absorption of a photon with sufficient energy, free charge carriers form in the three-dimensional lead halide perovskites.^{[65]–[67]} This is due to the low exciton (or bound electron-hole pair) binding energy E_B in these materials. Though the values for E_B differ per publication (from 2 to 62 meV^[68]), it is clear that the thermal energy at room temperature — about 25 meV — is sufficient for the formation of free charge carriers, as evidenced by experimental observation.

The free charge carriers that are generated upon photon absorption exhibit low effective mass for both electrons and holes. Due to the similar parabolicity of the dispersion relation of the conduction and valence band, the effective masses for electrons and holes are comparable for metal halide perovskites.^[69] In the case of MAPbI₃, the average values for the effective mass were calculated to be $0.19 m_0$ and $0.25 m_0$ for electrons (m_e) and holes (m_h), respectively.^[70] Here, m_0 is the free electron mass. The very similar values for m_e and m_h lead to ambipolar transport.^[69] This is reflected in the similarity in electron and hole diffusion lengths (see Equations 1.2 and 1.3) in these materials. The diffusion length is defined as:

$$L_D = \sqrt{D \tau}, \quad (1.2)$$

with τ the lifetime of the charge carrier, and the diffusion coefficient D defined as:

$$D = \frac{\mu k_B T}{q}. \quad (1.3)$$

Here, μ is the carrier mobility, k_B is the Boltzmann constant, T the absolute temperature and q the electrical charge of the carrier.^[71] In thin film form MAPbI₃ has a diffusion length of around 100 nm for both electron and holes, whereas a mixture of halides in conjunction with methylammonium and lead can result in values exceeding 1 μm .^{[72],[73]} Moreover, single crystalline MAPbI₃ has diffusion lengths of over 175 μm .^[74] These values are comparable to those of GaAs, where the diffusion lengths of the charge carriers range from about 10^0 to $10^1 \mu\text{m}$.^{[75],[76]}

This Section has shown that three-dimensional metal halide perovskites have many useful properties for optoelectronic applications. It should be noted that the scope of perovskites mentioned in this Section has so far been limited to the lead halides. However, the term three-dimensional metal halide perovskites encompasses all halide-based perovskites with other metal ions — such as Sn^{2+} ,^[14] Ge^{2+} ,^[77] or mixtures thereof^[78] — on the B-site in the ABX_3 structure. The research described in this thesis did not involve the use of other metal ions for three-dimensional perovskites, but to be thorough, the use of tin for photovoltaic applications should be mentioned.^[14]

It is clear that there is a myriad of possibilities to modify the composition of three-

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Figure 1.4: Schematic diagram of Ruddlesden-Popper perovskites, for $n = 1$ to 4. The diagram is based on a side view. The legend for the figure can be found on the right.

dimensional metal halide perovskites. Interestingly, inserting A-site cations that are too large according to the Goldschmidt tolerance factor can lead to the formation of two-dimensional phases with BX_6 octahedra: the so-called Ruddlesden-Popper phases. This class of materials is also referred to as two-dimensional perovskites.

1.1.2 Two-dimensional Ruddlesden-Popper perovskites

Two-dimensional Ruddlesden-Popper perovskites consist of two-dimensional perovskite layers with monovalent cations on either side. The general formula for this class of materials is $\text{A}_{n-1}\text{A}'_2\text{B}_n\text{X}_{3n+1}$. In this formula, n represents the number of inorganic octahedra in one layer, and A' is the long cation that surrounds the perovskite layer (see Figure 1.4). Each value of n leads to a material with distinct properties, due to the quantum confinement effect in these materials.^[23] When n is made very large ($n \rightarrow \infty$), one ends up with the three-dimensional equivalent. For this thesis the focus is on $n = 1$ compounds, which is the only form that does not have the smaller A cations.

Figure 1.5: Molecular structures of *n*-butylammonium and phenethylammonium.

These $n = 1$ compounds — which will be referred to as Ruddlesden-Popper perovskites — are characterized by two-dimensional planes of corner-sharing metal halide octahedra, separated by two A'^+ cations — hereafter referred to as A cations for simplicity — on either side (see Figure 1.4). This structure can be stacked to form a layered perovskite, with van der Waals interaction between the layers.^[79] Stacking takes place in a so-called staggered configuration, where the metal ions in the next layer are displaced with respect to the ones in the layer below, as to fit the cations between the inorganic layers.^[7] The space for the cation is no longer limited by the three-dimensional cage formed by the neighboring octahedra, and this means that larger cations can fit into the structure. The size limit can be approximated by calculating the ionic radius resulting in the maximum value of the Goldschmidt tolerance factor t for a perovskite structure: $t = 1$. If one uses lead ($R_{Pb} = 1.19 \text{ \AA}$) and iodine ($R_I = 2.20 \text{ \AA}$), this limit for R_A is about $2.59 \text{ \AA}$ (as per Equation 1.1).^[23] The use of a larger cation will not result in the formation a three-dimensional lead iodide perovskite. Of course, selecting smaller B- or X-site ions will decrease the size limit for A. Despite the lifted restriction on the size of the organic cation, there are still requirements for this ion. It needs to have at least one terminal group that is able to interact with the inorganic framework through ionic and hydrogen bonds, without the rest of the molecule interfering with the halides. Therefore, commonly used cations are based on primary amines.^[23] Examples of cations in two-dimensional lead halide perovskites are *n*-butylammonium and phenethylammonium (see Figure 1.5).^{[80],[81]}

Due to the aforementioned quantum confinement effect, two-dimensional perovskites have a higher exciton binding energy than their three-dimensional equivalents — E_B can be up to four times higher in a two-dimensional system^{[82],[83]}. Additionally, the difference in dielectric constant between the MX_4^{2-} -framework and the organic cations influences the exciton binding energy. Keldysh found that thin layers with a dielectric constant ϵ , surrounded by a medium with dielectric constant ϵ_1 , have a higher exciton binding energy if $\epsilon > \epsilon_1$.^[84] This effect was experimentally confirmed by Ishihara, who showed that changing

Figure 1.6: A type-I quantum well heterojunction, composed of an inorganic material between two organic layers with a larger bandgap.

the cation from decylammonium ($\epsilon = 3.39$) to phenethylammonium ($\epsilon = 4.41$) in a two-dimensional lead iodide perovskite decreases the exciton binding energy from 320 meV to 220 meV, respectively.^[85] From the order of magnitude of E_B it is clear that excitonic effects will manifest themselves at room temperature in these Ruddlesden-Popper phases, as opposed to the free charge carriers that are formed in three-dimensional lead halide perovskites.

Besides the increase in exciton binding energy, the quantum confinement effect also leads to higher bandgaps in Ruddlesden-Popper perovskites. The confinement is most pronounced in $n = 1$ compounds, and decreases with increasing n . Therefore, the lower the value of n , the higher the bandgap.^{[85],[86]} The quantum confinement effect in metal halide Ruddlesden-Popper perovskites is often explained by means of a type-I quantum well heterostructure with a finite barrier height. In such a structure, the conduction band of the inorganic layer is lower than that of the organic cation, and the valence band for the inorganic layer lies higher than that of the organic cation (see Figure 1.6). However, this approximation only holds for $n > 1$ materials; the bandgap for $n = 1$ perovskites is (severely) overestimated.^{[87],[88]} A solution for this was proposed by Even, Pedesseau and Katan, who treated the Ruddlesden-Popper phase not as two materials (the inorganic framework and the organic cation), but as a composite.^[87] This finding highlights the hybrid nature of this class of materials.

As in the case of the 3D perovskites, the bandgap of metal halide Ruddlesden-Popper perovskites is direct for various different metal ions, such as Pb^{2+} , Sn^{2+} and Cu^{2+} .^{[89]–[91]} The make-up of the band structure of two-dimensional lead- and tin-based halide perovskites is also similar to that of the three-dimensional equivalents: the anti-bonding M-s and X-p orbitals form the VBM, whereas the CBM consists of anti-bonding M-p and X-s orbitals — where the contribution from M is much larger than that of X.^{[92]–[94]} For other types of metals, such as the transition metals, this might not be true. An example is the ligand-to-metal charge transfer occurring in two-dimensional copper-halide perovskites. A more

detailed explanation on this subject will be given in Section 1.1.3. The similarities between lead- and tin-based Ruddlesden-Popper perovskites and three-dimensional perovskites in terms of band structure lead to analogous behavior when octahedral tilting is present: Knutson et al. reported that the Sn-I-Sn bond angle is a dominant factor in the electronic structure of tin-based Ruddlesden-Popper perovskites.^[95] As for the three-dimensional perovskites, the tilting leads to an increase of the bandgap.

The two-dimensional structure of Ruddlesden-Popper perovskites leads to anisotropy in the charge transport properties, since the organic cations act as insulating barriers. This hinders the charge transport in the out-of-plane direction, compared to that in the inorganic plane.^{[96],[97]} For lead- and tin-based perovskites, the effective masses of electrons and holes for the two-dimensional phases are similar to those of the three-dimensional equivalents.^{[94],[97]} Peng et al. found that two-dimensional lead iodide perovskite crystals have a sheet resistivity which is more than 10^3 times higher than that of three-dimensional MAPbI₃ crystals. This difference was explained by the lower amount of intrinsic shallow defects introduced in the two-dimensional crystals during their growth, leading to a lower amount of self-doping in the Ruddlesden-Popper perovskites.^[97] This could lead to lower electronic noise in optoelectronic devices.

A strong advantage of Ruddlesden-Popper perovskites over their three-dimensional counterparts is their higher stability. Smith et al. found that PEA gives two-dimensional perovskites a higher stability against moisture than MAPbI₃, owing to the hydrophobicity of the organic cation.^{[98],[99]} The ion migration that is known from three-dimensional perovskites is suppressed in Ruddlesden-Popper perovskites; Xiao et al. used density functional theory to calculate the formation energy of defects and concluded that it is significantly higher for two-dimensional perovskites.^[100] Therefore, the vacancy density is much lower than for three-dimensional perovskites, and as a result, the Ruddlesden-Popper are more stable in this respect.

Compared to the three-dimensional perovskites, Ruddlesden-Popper perovskites have distinctive advantageous properties, which depend on the composition of the material. It is clear that the entire class of two-dimensional metal halide Ruddlesden-Popper perovskites contains a very large number of possible compounds, owing to the variation of A, B and X elements. The work on Ruddlesden-Popper perovskites described in this thesis, reported in Chapters 4 and 5, is restricted to the copper-based perovskites. A member of the transition metal halide perovskite family, this class brings its own unique properties, due to the chemical nature of the Cu²⁺ d^9 ion. An interesting consequence of this d^9 state is the Jahn-Teller effect.

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Figure 1.7: The shape and orientation of the d -orbitals of the metal.

1.1.3 The Jahn-Teller effect in transition metal halide perovskites

As introduced in Section 1.1, metal halide perovskites consist of an inorganic octahedral network. The octahedral environment features a metal ion in the center, and is completed by bonding with six ligands — in this case, the halides. These ligands are located on the x -, y - and z -axes. Though the s - and p -orbitals of the metal participate in bonding with the ligands,^[101] we will focus on the influence of the d -orbitals (see Figure 1.7). Out of the five d -orbitals d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} , the first three will not bond with the ligands, since there is no net overlap with the ligand orbitals. The last two orbitals, $d_{x^2-y^2}$ and d_{z^2} , do overlap with those of the ligands and form bonding and anti-bonding molecular orbitals. The symmetry of these d -orbitals in the octahedral O_h point group can be assigned as follows: d_{xy} , d_{yz} and d_{xz} have t_{2g} symmetry, $d_{x^2-y^2}$ and d_{z^2} have e_g symmetry. Therefore, in an octahedral environment, the d -orbitals are split into two groups: the doubly degenerate e_g group and the triply degenerate t_{2g} group (see Figure 1.8). The energy between these two levels is defined as Δ_O , and this depends on the strength of the σ -interaction between the metal and the ligands. The value of Δ_O divides octahedral metal complexes into two categories: weak-field (small Δ_O) and strong-field (large Δ_O) complexes.^[101]

In 1937, Hermann Arthur Jahn and Edward Teller published their theorem on the lifting of degeneracy in a non-linear system by reducing its symmetry.^[103] This so-called Jahn-Teller effect was reformulated by Housecroft and Sharpe as: "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy".^[102] Due to the degeneracy in the e_g - and t_{2g} -orbitals, this effect can occur with the d -block transition metals, depending on the number of d -electrons and, possibly, on Δ_O . Comparing the value of Δ_O to the electron pairing energy, it might be energetically favorable to promote an electron to the

Figure 1.8: Splitting of the degenerate d -orbitals of a metal ion in an octahedral environment. a) The d -orbitals as a result of a spherical electrical field created by the ligands.^[102] When the charges of the ligands are located on the vertices of the octahedron, the fivefold degeneracy of the d -orbitals disappears: the orbitals split into two sets, as indicated in b).

Figure 1.9: Electron configuration of the d -orbitals for a) high-spin d^6 , b) low-spin d^6 , and c) d^9 metals.

higher e_g -level instead of pairing it with another electron in the t_{2g} -orbitals. This is called a high-spin case. The low-spin case is the opposite, i.e., the electron pairing energy is lower than Δ_O .^[102]

Three examples of d -block electron configurations are given in Figure 1.9. It is clear that a d^6 element can have different electronic configurations, depending on whether it is a high- or low-spin case, but for d^9 , e.g. Cu^{2+} , the configuration is always the same. Out of the three examples, only the low-spin d^6 configuration is nondegenerate. Therefore, this configuration cannot exhibit distortion due to the Jahn-Teller effect. In general, ions that have degeneracy in the filling of the e_g -level, such as the d^9 ion, typically have strong Jahn-Teller distortions. Degeneracy in the t_{2g} -orbitals, as is the case for high-spin d^6 , often leads to a much weaker effect.^[104]

The Jahn-Teller distortion that lowers the symmetry comes in two forms: elongation or compression of the octahedron (see Figure 1.10). This distortion is by definition in the z -direction and is the result of the electron configuration. For instance, in the case of d^9 , there are three electrons in the e_g -level: one of the two ($d_{x^2-y^2}$ or d_{z^2}) orbitals is filled completely,

Figure 1.10: The Jahn-Teller effect leads to a distortion in octahedral complexes, in the form of compression or elongation. The effect of compression and elongation of octahedral complexes on the energy levels of the metal ion is shown in the bottom row. The distortion is by definition in the z -direction; the x - and y -scales are not constant for all the cases.

while the other has one electron. In case of a completely filled $d_{x^2-y^2}$ -orbital, the repulsion between the metal and the ligands on the xy -plane is stronger, leading to an increase in bond length in the x - and y -direction, which compresses the octahedron. Elongation occurs when the d_{z^2} -orbital is completely filled; the higher electron density in the z -direction causes the bonds in this direction to elongate.^[105]

The distortion is caused by a reduction in energy for some orbitals in the octahedron. The affected orbitals are oriented in the direction of the longer metal-ligand bonds; the energy reduction is the result of lower overlap. That means that the $d_{x^2-y^2}$ and d_{xy} levels are lowered in the case of compression, and d_{z^2} , d_{xz} and d_{yz} are lowered when the octahedron is elongated.^{[105],[106]} A schematic illustrating the effect on the energy level diagram of the orbitals is shown in Figure 1.10.

Thus far, only the σ -interactions between the metal d -orbitals and ligand orbitals (s and p) have been considered. The full electron configuration depends on additional factors, such as the other metal orbitals and the π -interactions between the metal d -orbitals and

the ligand orbitals.^{[106],[107]} A thorough explanation would fall outside the scope of this introduction, however, understanding the effect of these bonds on the absorption spectrum of octahedral copper chloride complexes is useful for Chapter 4. After considering the σ - and π -interactions between the metal and the ligands, there are two types of transitions in the absorption spectrum: ligand-to-metal charge-transfer (LMCT) bands and $d \leftrightarrow d$ -transitions. The latter result from transitions between the partially filled d -orbitals of the metal, and are electronically forbidden — they break the Laporte selection rule — and are therefore low in intensity.^[106] The $d \leftrightarrow d$ -transitions have the lowest energy in the absorption spectrum. The LMCT takes place when an electron from a ligand orbital is promoted to one with primarily metal character.^[106] In the case of octahedral copper chloride complexes, the transfer is from either $\text{Cl}^- p\sigma$ or $\text{Cl}^- p\pi$ to the half-filled $\text{Cu}^{2+} d_{x^2-y^2}$ -orbital.^[107] Given that $\text{Cl}^- p\sigma$ is lower in energy, the former transition takes place at shorter wavelengths.

1.2 Applications of metal halide perovskites in devices

The properties of metal halide perovskites can vary significantly owing to their tunable composition. The versatility of the class of materials allows them to be exploited for various types of devices. Most of these devices are of the optoelectronic type, such as photodetectors and light-emitting diodes.^{[8],[10],[24],[26]} The most common application of metal halide perovskites is in solar cells. Chapter 3 describes the use of MAPbI_3 for photovoltaic applications. The necessary theory is introduced in Section 1.2.1. Another type of application is the detection of gases and vapors with perovskites, which will be described in Section 1.2.2 and Chapter 5.

Despite the different applications, most of these devices are made with solution processing techniques, which can be used to produce thin films or single crystals. Spin coating and blade coating are widely used to produce perovskite thin films. The fact that these techniques can be used at low temperatures means that a wide variety of substrates can be used for devices, which shows their versatility. There are also downsides to solution processing. For instance, the morphology is strongly influenced by factors such as the choice of solvent(s), processing technique, and annealing conditions.^[108] The morphology also determines the quality of the perovskite film, as traps can be introduced in the form of grain boundaries, for example.^[109] Therefore, the processing conditions have to be carefully selected to result in a favorable morphology for the device of one's choice.

1.2.1 Perovskite solar cells

The first reported perovskite solar cell was made by Kojima et al. in 2009.^[11] They used two perovskites, of which MAPbI₃ was the most promising, with a power conversion efficiency (PCE) of 3.8%. Nowadays,ⁱ the PCE of perovskite solar cells is over 25%.^[110] The PCE of a solar cell is defined as the ratio of the output of electrical power to the power of the incident light. In 1961, William Shockley and Hans-Joachim Queisser calculated the maximum theoretical PCE of a single layer solar cell to be 30%, based on a photoactive layer with a bandgap of 1.1 eV and a 6000 K blackbody spectrum.^[111] This approximation was improved upon by Sven Rühle, who used the AM1.5G spectrum — the international standard for solar cell testing — instead of the blackbody spectrum. As a result, two local maxima appeared in the curve of PCE versus bandgap: one at 1.15 eV (32.9%) and one at 1.34 eV (33.2%).^[43] The latter value is reasonably close to the bandgap of MAPbI₃ (1.55 eV); Rühle calculated that the maximum PCE for semiconductors with bandgaps between 1.3 and 1.6 eV is higher than 30%.

Apart from a suitable bandgap, metal halide perovskites have several other beneficial properties for photovoltaics. Examples are the high charge carrier diffusion lengths and optical absorption coefficient (see Section 1.1.1). This combination allows for the use of thin films of hundreds of nanometers,^{[13],[112],[113]} to ensure strong absorption of the incident light without losing charge carriers due to recombination. The charge carriers generated by exciting the perovskite need to be extracted in order to produce electrical power. This is done by two charge transport layers: one for electrons, the electron transport layer (ETL) or n-type layer, and one for holes, the hole transport layer (HTL) or p-type layer. The HTL (ETL) transports the holes (electrons) to the anode (cathode). The two electrodes finish the device. One of them needs to be transparent in order to let light pass through to the perovskite layer; metal oxides (such as indium-doped tin oxide, or ITO) are typically used for this purpose. This transparent electrode is deposited directly on a glass substrate. The electrode on the other end of the solar cell is typically a thin metal layer. Depending on which layer is deposited on the transparent electrode, one can have two device configurations: the p-i-n and the n-i-p configuration, where i represents the perovskite active layer (see Figure 1.11).

In order to transport charge efficiently, and to prevent unwanted recombination, there are requirements for the energy levels of the HTL and ETL with respect to the perovskite layer. They need to accept the charge carriers they are designated to transport and block the opposite type, i.e. there should not be energy barriers between the perovskite and the transport layers for the carriers that they should transport.^[114] This means that the energy level of the ETL should be lower than the CBM of the perovskite, and that the HTL's energy

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ⁱAs of February 2021

Figure 1.11: Schematics of perovskite solar cells in the n-i-p and p-i-n configuration.

Figure 1.12: Energy level diagram of a perovskite solar cell.

level ought to lie higher than the perovskite's VBM (see Figure 1.12). Another requirement for the transport layers is that they transport charge efficiently — they should have a high charge carrier mobility. If the charge transport is poor, the carriers from the transport layer can recombine with charges in the perovskite layer.^[114] Finally, it is important to have proper energy level alignment between the transport layers and the respective electrodes. It is favorable to have ohmic contact between them to facilitate the injection of charges.^[114]

Physics of solar cells

The working mechanism behind a solar cell relies on the Shockley diode equation, which describes the current flowing through a p-n junction:

$$I = I_s \left(e^{\frac{qV}{nkT}} - 1 \right), \quad (1.4)$$

Figure 1.13: Example of a $J - V$ scan for a solar cell. The maximum power point is found at the red circle. The ratio of the area of the blue rectangle to the total area of the curve is equal to the fill factor.

where I_s is the reverse saturation current of the diode, q is the elementary charge, V is the voltage across the diode, k is the Boltzmann constant, T the absolute temperature and n the ideality factor of the diode. A diode with n equal to 1 is called an ideal diode. When photons of sufficient energy fall on the semiconductor, they excite the charge carriers, leading to a current I_L . This modifies Equation 1.4 to

$$I = I_s \left(e^{\frac{qV}{nkT}} - 1 \right) - I_L. \quad (1.5)$$

Equation 1.5 describes the $I - V$ characteristics of a solar cell.^[71] The current I_L depends on the total area A that can absorb photons, therefore, it is customary to normalize Equation 1.5 with respect to A to obtain the current density J :

$$J = \frac{I}{A} = J_s \left(e^{\frac{qV}{nkT}} - 1 \right) - J_L. \quad (1.6)$$

Figure 1.13 shows the $J - V$ dependence in a graph. Power is generated in the fourth quadrant of the graph; the maximum power point (MPP) is found there, where the product of J and V is largest. The power conversion efficiency (η , or PCE) is defined as the ratio of the maximum power P_{MPP} and the incoming power P_{in} :

$$\eta = \frac{P_{MPP}}{P_{in}} \times 100\% = \frac{V_{MPP} J_{MPP}}{P_{in}} \times 100\% \quad (1.7)$$

Equation 1.7 gives the definition of η in terms of P_{MPP} . In practice, solar cell researchers almost always refer to three other parameters to compare performance: the short-circuit current density J_{SC} , the open-circuit voltage V_{OC} and the fill factor (FF). The J_{SC} is the

Figure 1.14: Equivalent circuits of a) an ideal solar cell and b) a solar cell with shunt resistance R_{SH} and series resistance R_S .

current density at 0 V, and the V_{OC} is defined as the voltage that, when applied to the solar cell, leads to no current. This voltage is a result of the difference in the quasi-Fermi levels for electrons and holes, which occurs after photoexcitation.^[115] The fill factor is defined as

$$FF = \frac{P_{MPP}}{J_{SC} V_{OC}} \times 100\%, \quad (1.8)$$

and is represented by the ratio of the area of the blue rectangle in Figure 1.13 to the total area under the $J - V$ curve. The fill factor is typically reported as a percentage. From Equations 1.7 and 1.8 it is clear that η can be calculated by

$$\eta = \frac{J_{SC} V_{OC} FF}{P_{in}} \quad (1.9)$$

With Equation 1.9, the relation between PCE and the three main parameters J_{SC} , V_{OC} and FF is explained. To understand how these parameters are affected, a model of the solar cell is needed. An equivalent circuit representing an ideal solar cell is shown in Figure 1.14a. Here, the photocurrent I_L is included as a current source. Figure 1.14b depicts a more realistic circuit, with additional resistances inserted into the circuit: the shunt resistance R_{SH} and the series resistance R_S . The former should be high ($R_{SH} \rightarrow \infty$) to prevent leakage current due to alternative pathways in the device, and the latter is zero in the ideal case, to minimize the voltage loss over the device. The series resistance is a combination of the resistance of the various layers and the contact resistance at their interfaces. Both R_{SH} and R_S affect the FF in a negative way if they deviate from their ideal values.^[71] One can extract information about these resistances by looking at the slope of the $J - V$ characteristics at $V = 0$ (R_{SH}) and $V = V_{OC}$ (R_S), considering $\frac{dJ}{dV} \propto \frac{1}{R}$.

Interestingly, perovskite solar cells are known to suffer from a hysteresis in the current density-voltage characteristics. This behavior is exhibited when one compares the forward ($0 V \rightarrow V_{OC}$) to the reverse ($V_{OC} \rightarrow 0 V$) scan, though not every device is susceptible to

the effect.^[116] Ion migration, as explained in Section 1.1.1, is considered to be a probable cause of the hysteresis. Eames et al. proposed that the migrated ions screen the electric field in the device, thereby reducing the collection efficiency of photogenerated charges.^[117] In spite of this straightforward theory, it cannot be the only explanation for the hysteresis observed in perovskite solar cells, because not every device displays hysteresis. Therefore, researchers looked for another likely cause, and found it in the form of charge trapping and detrapping.^{[116],[118]} In this case, they specifically refer to the deep trap states which can get filled with electrons and holes during the forward scan. These charge carriers can subsequently be released under short-circuit conditions.^[118] It should be noted that the current knowledge on hysteresis is not fully satisfactory, and the underlying mechanisms might be more complex.^[118]

The presence of trap states can lead to recombination. One can make the distinction between band-to-band recombination and trap-assisted recombination (also called Shockley-Read-Hall recombination), where the latter should be minimized as this is detrimental to the device efficiency. A technique used to discern between these types of recombination is based on the light intensity dependence of the V_{OC} . When Equation 1.6 is rewritten in terms of the open-circuit voltage, for which $J(V = V_{OC}) = 0$, one gets

$$V_{OC} = \frac{nkT}{q} \ln \left(\frac{J_L}{J_s} + 1 \right). \quad (1.10)$$

This means that plotting V_{OC} versus the light intensity in a semi-logarithmic plot should give a slope of $\frac{nkT}{q}$, assuming that the photocurrent J_L is linearly dependent on the light intensity.ⁱⁱ^[120] The ideality factor n can be extracted from this slope. According to classical theory, when n is equal to 1, the device exhibits only second-order recombination (i.e. band-to-band recombination). In case n is equal to 2, first-order recombination (such as trap-assisted recombination) dominates.^[121] A value in between 1 and 2 is attributed to a superposition of the two mechanisms.^[122] However, reports on the light intensity dependence of the V_{OC} of perovskite solar cells have undermined these conclusions. Caprioglio et al. found that an ideality factor of 1 can be caused by recombination at the interface instead of band-to-band recombination, especially if the device has a low V_{OC} .^{[122],[123]} They came to the counterintuitive conclusion that a higher ideality factor might actually indicate a better device.^[122] An ideality factor of 1 would only be beneficial if the interfacial recombination is suppressed. Therefore, it seems that the conclusions from traditional theory on the V_{OC} light intensity dependence have to be used with care: if the recombination in the device is dominated by surface recombination, the theory does not hold.^{[122],[123]} A strong indication of this is that the open-circuit voltage of the device is low.

ⁱⁱFor an example of this linear dependence in the case of perovskites, see the work of Shao et al.,^[119] for instance.

The $J - V$ characteristics of a solar cell provide a wealth of information about the device, such as PCE, J_{SC} and V_{OC} , and allow for qualitative comparison of R_{SH} and R_S between different cells. The limitation of $J - V$ measurements is that they are carried out with an AM1.5G spectrum light source, which means that any spectral dependence is overlooked. This information can be obtained with external quantum efficiency (EQE) measurements, and this is often used to check the J_{SC} obtained by the $J - V$ scans. The EQE is the ratio of collected charge carriers to the number of incident photons for a certain wavelength, and can be calculated as follows:

$$EQE(\lambda) = \frac{hc}{\lambda q} \frac{J(\lambda)}{P_{in}(\lambda)} \times 100\%, \quad (1.11)$$

where h is Planck's constant, c the speed of light in vacuum, q the elementary charge, λ the wavelength of the photon, $J(\lambda)$ the short-circuit current density at that wavelength, and $P_{in}(\lambda)$ the light intensity at that wavelength.

Equation 1.11 explains the need for a monochromatic light source for the EQE measurements. This is often done by filtering the light from a white-light source with narrow bandpass filters. By varying the filters, a complete spectrum from the absorption onset around the bandgap up until the ultraviolet can be obtained. Since every data point is based on the short-circuit current density $J(\lambda)$, integration over the entire spectrum gives the total J_{SC} as measured in the $J - V$ experiment, if the light intensity of the AM1.5G spectrum $P_{AM1.5}(\lambda)$ is taken into consideration:

$$J_{SC,calc} = \int \frac{\lambda q}{hc} \frac{EQE(\lambda)}{100\%} P_{AM1.5}(\lambda) d\lambda, \quad (1.12)$$

The value of $J_{SC,calc}$ obtained with Equation 1.12 can be used to compare the value of J_{SC} from the $J - V$ characteristics to verify the validity of the results.

1.2.2 Gas and vapor sensors

The detection of toxic or other hazardous gases and vapors is essential to guarantee safety at the workplace and a healthy living environment in terms of air quality. Highly sensitive sensors are needed to measure the concentration of various gases and vapors, because the safety limits for these compounds can be on the order of parts per million (ppm).

For decades, scientists have been developing gas sensors, leading to many different categories such as solid electrolyte,^[124] electrochemical,^[125] infrared absorption,^[126] paramagnetic,^[127] and metal oxide semiconductor sensors.^[128] This last type of device is highly sensitive, small, and cost-effective compared to traditional techniques.^[129] The so-called resistor metal oxide semiconductor gas sensors consist of a metal oxide semiconductor, such as SnO_2 ,

1.3. THESIS OUTLINE

whose resistivity changes when it is exposed to a certain gas.^[129] Consequently, the presence of the gas can be detected by monitoring the resistance of the sensor. This effect is observed at elevated temperatures on the order of hundreds degrees Celsius,^{[129],[130]} and is based on chemical catalytic reactions between the gas and the oxide surface, leading to a change in conduction.^[131]

The elevated temperatures involved in the gas detection with metal oxides lead to a process with a high energy demand, and having a low-temperature alternative would be desirable. This alternative could come from the field of metal halide perovskites. One downside of lead halide perovskites is their instability in air, which was already mentioned in Section 1.1.1, but in 2015, Grancini et al. were able to exploit this disadvantage.^[132] They found that the photoluminescence (PL) wavelength of a MAPbI₃ single crystal blueshifted when it was exposed to 50% relative humidity, and by doing so, demonstrated a rudimentary humidity sensor. One year later, Fang et al. showed an increase in PL intensity for MAPbBr₃ single crystals upon exposure to humidity or oxygen.^[15] This is the result of the passivation of surface trap states by the water and oxygen molecules. Furthermore, they utilized this effect in a resistor-type sensor, which showed improved conduction upon exposure to air.

Apart from water and oxygen, metal halide perovskites were used to detect various other substances. Zhao and Zhu found an optical response (bleaching) of MAPbI₃ to ammonia.^[133] Detection of hydrogen chloride by CsPbBr₃ nanocrystals is also based on an optical effect: the PL blueshifts.^[134] Examples of resistor-type sensors include the study of Zhuang et al., who demonstrated that the conductance of CH₃NH₃PbI_{3-x}(SCN)_x films increases significantly when it is brought into contact with acetone vapors or nitrogen dioxide.^[135] Another example is the ability of CH₃NH₃PbI_{3-x}Cl_x films to detect ozone on a parts per billion scale.^[136]

Though lead halide perovskites can detect a number of gases and vapors, one should keep in mind that some of these compounds might damage the perovskite layer. Aside from the degradation caused by humidity,^[137] acetone vapors have been proven to dissolve the organic molecule in MAPbI₃.^[138] Zhao and Zhu found that the optical bleaching effect of MAPbI₃ during exposure to ammonia is not reversible when the exposure lasts for tens of minutes.^[133] Due to the instabilities that characterize the three-dimensional lead-based perovskites (see Section 1.1.1), we shifted our focus to the more stable two-dimensional perovskites for vapor sensing applications, as will be addressed in Chapter 5.

1.3 Thesis outline

This thesis combines fundamental research on metal halide perovskites with work on their application in devices. The different perovskites that were used in the Chapters lend themselves to a division of the thesis into two parts.

The first part, encompassing *Chapters 2 and 3*, is dedicated to the three-dimensional lead

halide perovskites. *Chapter 2* describes the optimization of p-i-n perovskite solar cells by varying the electron transport layer. *Chapter 3* compares the photophysics and phase purity of cesium-based lead halide perovskites in the form of thin films and single crystals.

The second part consists of *Chapters 4* and *5*. Here, the focus is shifted to the copper-based two-dimensional Ruddlesden-Popper perovskites. *Chapter 4* describes the photochromism (a light-induced color change) that $(\text{PEA})_2\text{CuCl}_4$ exhibits upon illumination with ultraviolet (UV) light. *Chapter 5* utilizes this phenomenon, by incorporating UV-treated $(\text{PEA})_2\text{CuCl}_4$ into an alcohol vapor sensor.

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CHAPTER 2

Metal Halide Perovskite Solar Cells With PTEG-1 as Electron Transport Layer: Improved Charge Dynamics Leading to Higher Power Conversion Efficiencies

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In this chapter we present p-i-n type perovskite solar cells using NiO_x as the hole transport layer and a fulleropyrrolidine with a triethylene glycol monoethyl ether side chain (PTEG-1) as electron transport layer. This electron transport layer leads to higher power conversion efficiencies compared to perovskite solar cells with PCBM (phenyl- C_{61} -butyric acid methyl ester). The improved performance of PTEG-1 devices is attributed to the reduced trap-assisted recombination and improved charge extraction in these solar cells, as determined by light intensity dependence and photoluminescence measurements. Through optimization of the hole and electron transport layers the power conversion efficiency of the NiO_x /perovskite/PTEG-1 solar cells was increased up to 16.1%.

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2.1 Introduction

Hybrid inorganic-organic perovskite solar cells have attracted considerable attention because of their high power conversion efficiencies, owing to their strong absorption over a wide range of the solar spectrum, high diffusion lengths for electrons and holes and ambipolar charge transport characteristics.^{[1]–[6]} These solar cells have been reported both in the n–i–p and in the p–i–n structure. However, n–i–p type planar cells, where the perovskite layer is sandwiched between TiO₂ and the hole transport layer, suffer from severe hysteresis, as opposed to p–i–n cells.^{[7]–[9]} A commonly used hole transport layer (HTL) in p–i–n solar cells is poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). However, perovskite solar cells with this HTL typically have a lower open-circuit voltage (V_{OC}) than the cells based on TiO₂.^[8] In addition, solar cells incorporating PEDOT:PSS are sensitive to degradation, which is detrimental for long-term operation.^[10]

Inorganic materials, such as metal oxides, are more stable alternatives as HTLs, because they are less prone to degradation under a variety of conditions.^{[11]–[13]} NiO_x is an example of an inorganic HTL with good chemical stability and suitable work function (−4.8 eV) for p–i–n perovskite solar cells.^{[14],[15]} The V_{OC} of NiO_x-based perovskite solar cells is typically higher than that of PEDOT:PSS devices (1 V and 0.9 V, respectively), leading to higher power conversion efficiencies.^{[15],[16]}

PCBM (phenyl-C₆₁-butyric acid methyl ester) is commonly used as the electron transport layer in the p–i–n structure, but this material is often combined with other layers, such as bathocuproine (BCP), to block holes and improve the power conversion efficiency.^{[15],[17],[18]} Incorporating additional layers into the solar cell’s device structure leads to increased complexity in processing, and therefore it is desirable to replace the electron transport layer to simplify the overall device structure. Recently, Yin et al. showed NiO_x-based solar cells with only PCBM as the ETL, reaching a power conversion efficiency (PCE) of 15.7%.^[19] However, their solar cells have a V_{OC} lower than 1 volt, which limits their efficiency. Our previous work on PEDOT:PSS-based p–i–n perovskite solar cells demonstrated that the PCE increases when PCBM is replaced by PTEG-1, which is a fulleropyrrolidine with a triethylene glycol monoethyl ether side chain.^{[9],[20]}

In this chapter, we report the first use of PTEG-1 in perovskite solar cells with a NiO_x hole transport layer. We compare the performance of solar cells with PTEG-1 to PCBM-based devices and conclude that the use of PTEG-1 can lead to higher PCEs up to 16.1% with open-circuit voltages as high as 1.12 V.

Figure 2.1: a) Schematic device structure of a perovskite solar cell; the stacking is: ITO/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /ETL/Al. b) Chemical structures of PCBM and PTEG-1, which are used as ETLs.

2.2 Results and discussion

The device structure used in this work is ITO/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /ETL/Al, as shown in Figure 2.1a. The chemical structures of the two materials used as ETLs, PCBM and PTEG-1, are displayed in Figure 2.1b. The perovskite layer is deposited from a mixture of high boiling point solvents, based on the method reported by Jeon et al.^[6] Figure 2.2 displays the scanning electron microscopy (SEM) images of a uniform and pinhole-free perovskite film deposited on a NiO_x film. The perovskite grains are extremely large (on the order of tens to hundreds of microns) and the surface is completely covered.

Figure 2.3a shows the current density–voltage (J - V) characteristics of the solar cells with PTEG-1 and PCBM as electron transport layers under AM1.5G illumination. The J - V parameters are summarized in Table 2.1. The solar cell with PCBM reaches 11.8% power conversion efficiency, with a short-circuit current density (J_{SC}) of 19.6 mA/cm^2 , an open-circuit voltage of 1.09 V and a fill factor (FF) of 55%. When PTEG-1 is used instead of PCBM, the V_{OC} and J_{SC} increase to 1.11 V and 21.4 mA/cm^2 , respectively. This results in a higher PCE of 13.1%, since the fill factor does not change.

Our group has previously reported improvements in V_{OC} and J_{SC} after replacing PCBM by PTEG-1 in hybrid perovskite devices using PEDOT:PSS as the hole extraction layer. This improvement was attributed to the reduction of trap-assisted recombination in the case of PTEG-1.^[9] We carried out light intensity dependence measurements to determine the reason for the increased performance in the current device structure and the results are displayed in Figure 2.4. The dependence of V_{OC} on the light intensity should be linear when plotted in a semi-logarithmic scale, which is the case in Figure 2.4. We can extract the diode ideality factor n (in units of kT/q , where k is Boltzmann's constant, T is the absolute temperature and q the elementary charge) from the slope of the fit. When n is equal to 1,

Figure 2.2: Scanning electron microscopy image of perovskite film on a NiO_x substrate.

Figure 2.3: a) J - V curve for different ETLs in the glass/ITO/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /ETL/Al device structure. b) EQE spectra of the devices in (a). The layer thicknesses of NiO_x , perovskite, PCBM and PTEG-1 are 40 nm, 270 nm, 65 nm and 60 nm, respectively.

Figure 2.4: Light intensity dependence of the V_{OC} of the solar cells in Figure 2.3. The lines are the fits of the data.

only bimolecular recombination takes place in the device. Trap-assisted recombination is characterized by n between 1 and 2.^[21] In our case, the values of n for PCBM and PTEG-1 are 1.37 and 1.21, respectively. This indicates that the trap-assisted recombination is lower in the case of PTEG-1.ⁱ Figure 2.3b shows the external quantum efficiency (EQE) spectra of the ITO/ NiO_x /perovskite/ETL/Al devices for both PCBM and PTEG-1. The EQE of the PTEG-1 device is higher than 80% over almost the entire wavelength range from 420 to 660 nm, and it is higher than that of PCBM over the full range of the measurement. The J_{SC} obtained by integration of the EQE spectra is in agreement with the J_{SC} obtained from the J - V measurements for both ETL layers (17.6 and 20.2 mA/cm^2 for PCBM and PTEG-1, respectively).

Table 2.1: Device performances for different ETLs.

ETL	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
PCBM	19.6	1.09	55	11.8
PTEG-1	21.4	1.11	55	13.1

To fully understand why our PTEG-1 solar cells perform better than the PCBM-based devices we conducted photoluminescence (PL) measurements (see Figure 2.5). With these measurements it is possible to study the charge carrier recombination upon excitation. The steady state PL was measured for stacks composed of glass/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM and glass/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PTEG-1; the structure glass/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ was used as comparison. From the measurements in Figure 2.5a it is clear that there is successful charge

ⁱThis is the conclusion drawn in the original article. However, recent publications have made it clear that the traditional theory on the ideality factor might not always be true for perovskites (see Section 1.2.1). In spite of this new insight, the conclusion of this article — that PTEG-1 is a better ETL — is still valid.

Figure 2.5: a) Steady state PL spectra for glass/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ (black line), glass/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PCBM (red line) and glass/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PTEG-1 (blue line). b) Time-resolved PL of the samples in (a). Symbols show the data, the solid lines are the mono-exponential fits.

transfer from the perovskite layer to the ETLs, as indicated by the quenched PL signal. The quenching in the PTEG-1 sample is stronger than in the PCBM sample, which is supported by the time-resolved PL data shown in Figure 2.5b. This plot shows that the PL signal decays mono-exponentially for all samples. The lifetime of the PL signal is shorter for PTEG-1 ($\tau = 10.3$ ns) than for PCBM ($\tau = 25$ ns) and for the perovskite only ($\tau = 190$ ns). These results indicate that the charge extraction is better in the case of NiO_x /perovskite/PTEG-1 than in the case where PCBM is the ETL.

In order to improve the power conversion efficiency of the PTEG-1 solar cells, we attempted to optimize the thicknesses of the transport layers. Solar cells with different thicknesses of the PTEG-1 layer were made and the corresponding J - V measurements are presented in Figure 2.6a and in Table 2.2. It was found that when the PTEG-1 layer is thin (about 35 nm), the devices show current leakage. As a result the fill factor is low, which could be due to insufficient coverage of PTEG-1 on the perovskite surface. Increasing the PTEG-1 thickness improves the FF and PCE considerably. The device with 50 nm PTEG-1 has a fill factor of 61%, but increasing the thickness further (60 nm) lowers the FF to 56%. Therefore, 50 nm is the optimal thickness for this ETL. Below this thickness, there is the possibility of shunt pathways. However, above 50 nm there will be additional series resistance in the layer, which reduces the PCE.

Figure 2.6b shows the effect of the NiO_x thickness on the device performance; a slight change in the thickness has a large influence on the device performance. The thickness of the perovskite layer was 270 nm, the same as used in the cells from Figure 2.6a, and the

Figure 2.6: a) J - V curves of glass/ITO/NiO_x/CH₃NH₃PbI₃/PTEG-1/Al devices with different thicknesses of the PTEG-1 layer. b) J - V measurements showing the influence of the thickness of NiO_x on the device performance. The perovskite and PTEG-1 thicknesses in these devices are 270 and 50 nm, respectively

Table 2.2: Device performances for different thicknesses of PTEG-1 based on the structure glass/NiO_x (30 nm)/CH₃NH₃PbI₃ (270 nm)/PTEG-1/Al.

PTEG-1 thickness (nm)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
35	21.7	1.10	39	9.4
50	21.3	1.11	61	14.4
60	21.9	1.10	56	13.6

PTEG-1 layers were 50 nm thick. The current density – voltage parameters are listed in Table 2.3. It is evident that thicker layers lead to an increase in V_{OC} (from 0.99 to 1.14 V). The short-circuit current density and fill factor for the device with 20 nm NiO_x are 20.2 mA/cm² and 47%, respectively. When the thickness of the NiO_x layer is increased to 40 nm, both J_{SC} and FF increase. However, increasing the thickness beyond 40 nm does not lead to an overall better device performance, which is mainly caused by a reduction in the fill factor. This trend can be explained by the increased series resistance in the HTL. We can conclude here that the optimal thickness for NiO_x is 40 nm, and this gives a solar cell with a J_{SC} of 22.9 mA/cm², a V_{OC} of 1.12 V, a FF of 63% and a resulting PCE of 16.1%. This is among the highest reported values for a NiO_x/perovskite/fullerene solar cell. The value of 16.1% is the maximum value that we achieved; the J - V curves of this device are shown in Figure 2.7. The reader is referred to the original publication for statistics of the power conversion efficiencies for all devices in the same batch.

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Figure 2.7: The J - V scans of the champion cell of 16.1% PCE in forward and reverse direction.

Table 2.3: Device performances for different thicknesses of NiO_x for a device structure of glass/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ (270 nm)/PTEG-1 (50 nm)/Al.

NiO_x thickness (nm)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
20	20.2	0.99	47	9.4
40	22.9	1.12	63	16.1
60	20.9	1.13	58	13.6
80	21.1	1.14	52	12.5

2.3 Conclusions

In summary, we have demonstrated that the power conversion efficiency of NiO_x -based p-i-n planar perovskite solar cells can be improved by changing the electron transport layer from PCBM to PTEG-1. This is mainly caused by the increased short-circuit current density when PTEG-1 is used. External quantum efficiency and photoluminescence measurements indicate that the charge extraction is more efficient for devices with PTEG-1 as ETL. In addition, we found that the solar cells with PTEG-1 suffer less from trap-assisted recombination compared to the PCBM counterparts. Optimization of the thicknesses of both the electron and hole transport layer led to power conversion efficiencies up to 16.1% for ITO/ NiO_x / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /PTEG-1/Al.

2.4 Methods

Materials and reagents

All solvents and reagents were of analytically pure quality and used as received. PbI_2 (99.99% purity) and MAI (98% purity) were purchased from TCI. Nickel formate dihydrate and dimethylsulfoxide (DMSO) were bought from Alfa Aesar. γ -butyrolactone (GBL), ethylene glycol, chlorobenzene and ethylenediamine were purchased from Sigma Aldrich. PCBM (99.5%) was purchased from Solenne BV. PTEG-1 was prepared by our published procedure.^[20]

Synthesis of NiO_x solution and spin coating of thin film

The precursor for NiO_x film coating was prepared with 1 M nickel formate dihydrate in ethylene glycol solution containing 0.75 M ethylenediamine, passed through a $0.45\ \mu\text{m}$ PTFE filter. Patterned ITO-coated glass substrates were ultrasonically cleaned with soapy water, deionized water, acetone and isopropanol, followed by oxygen plasma treatment for 2 minutes. The solution was spin coated on the glass/ITO substrate at 4000 rpm for 80 seconds and dried for 60 seconds at 120°C , resulting in a 40 nm thick layer. Then, the substrate was annealed at 300°C in an oven in ambient atmosphere for 60 minutes.

Device fabrication

All processes (except the fabrication of the NiO_x film) were carried out inside a nitrogen-filled glovebox, with oxygen and moisture levels below 1 ppm. The perovskite solution was prepared by dissolving lead iodide and methylammonium iodide in GBL:DMSO (volume ratio 7:3) with a concentration of 1 M. This solution was stirred over night at room temperature. The perovskite precursor solution was deposited onto a glass/ITO/ NiO_x substrate by a one-step spin coating process at 1000 rpm for 40 seconds, based on the method of Jeon et al.^[6] The anti-solvent treatment in their method was not used and this results in very large perovskite grains with a relatively rough surface. The film, with a thickness of 270 nm, was further annealed on a hotplate at 100°C for 3 min. After the perovskite film was cooled down to room temperature, a 20 mg/mL PCBM or 11 mg/mL PTEG-1 solution in chlorobenzene was spin coated on the perovskite layer at 800 rpm for 60 seconds for the cells in Figure 2.3. The optimized PTEG-1 layer was spin coated at 1000 rpm for 60 seconds. Finally, the aluminium electrode (100 nm thickness) was thermally evaporated at a pressure of 1×10^{-7} mbar using an evaporation mask on top of the ETL.

Solar cell characterization

The current density-voltage characteristics of the solar cells were measured under simulated AM1.5G solar illumination from an Osram HMI 1200W/DXS lamp. The light intensity was set to $100\ \text{mW}/\text{cm}^2$, calibrated by a silicon reference cell. J - V scans were carried out over

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the voltage range from -0.4 to 1.4 V in steps of 40 mV. The solar cells were measured after 20 minutes continuous illumination at room temperature. Thickness optimization was done by making at least 15 samples per variation. For the light intensity dependence measurements a set of neutral density filters was used to attenuate the illumination intensity.

External quantum efficiency measurements were carried out with monochromatic light under short-circuit conditions. A set of band pass filters with full width at half maximum of 10 ± 2 nm were used for the monochromatic light. The light source was a 250 W quartz tungsten halogen lamp (Osram 64655 HLX).

Photoluminescence measurements

For the PL measurements, the second harmonic (400 nm) of a mode-locked Ti:sapphire laser (Mira 900, Coherent) was used as excitation source. The laser power was attenuated to 100 μ W using neutral density filters. Fluorescence was collected into a spectrometer with a 50 lines/mm grating and recorded by a cooled EM-CCD camera (ImagEM, Hamamatsu). Time-resolved traces were recorded with a Hamamatsu streak camera working in single sweep mode. A pulse picker was used to for reducing the repetition rate of the laser. Lifetimes were fitted using exponential functions, the best fit could be achieved with a mono-exponential function. Two decay components could be observed in TRPL measurement at higher photoexcitation density. However, in our case, the power used is around 0.76 mJ, which is too low to see the fast decay in time-resolved photoluminescence.

Morphological characterization

The surface morphology was imaged using a scanning electron microscope (Philips/Fei, XL30-ESEM) operated in high vacuum mode, with an accelerating voltage of 5 kV. Since the samples were conductive enough no additional treatment was necessary.

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CHAPTER 3

Stable Cesium Formamidinium Lead Halide Perovskites: A Comparison of Photophysics and Phase Purity in Thin Films and Single Crystals

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The stability of the active layer is an underinvestigated aspect of metal halide perovskite solar cells. Furthermore, the few articles on the subject are typically focused on thin films, which are complicated by the presence of defects and grain boundaries. In this chapter, a different approach is taken: a perovskite composition that is known to be stable in single crystal form is used, and its (photo-)physical properties are studied in the form of spin-coated thin films. The perovskites are lead-based with cesium and formamidinium as the A-site cations and iodide and bromide as the halide anions, with the formula $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{3-x}\text{Br}_x$. These compounds show high potential in terms of stability in single crystal form and closely resemble the compounds that have successfully been used in highly efficient perovskite–silicon tandem solar cells. It is found that a small difference in bromine content ($x = 0.45$ vs 0.6) has a significant impact in terms of the phase purity and charge carrier lifetimes, and conclude that the thin films of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ have good potential for the use in optoelectronic devices.

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3.1 Introduction

The main strength of hybrid metal halide perovskite solar cells is their high power conversion efficiency, which can reach values over 25%.^[1] However, an underdeveloped aspect of these devices is their stability, for which further investigation and improvement are needed. One of the most important aspects considered for improvement is the structural stability of the perovskite layer, which is influenced by the stoichiometry of the material and, therefore, also affects the environmental stability of the device.^{[2]–[5]} A perovskite with low structural stability can be affected by degradation, for example, in the form of phase segregation.^[6]

An approach to improve the structural stability is to use elaborate compositions involving multiple cations or halide ions based on the Goldschmidt tolerance factor, which will be addressed later.^{[5],[7]–[9]} The caveat with this method is that, generally, perovskite solar cells are based on thin films. This brings more factors into the equation: the morphology of the layer and the presence of defects.

The solution processes used to make perovskite thin films introduce defects into the layer, for example, in the form of grain boundaries, which have been correlated with the material's instability.^[10] The choice of solvent, the use of antisolvent, and the processing method can all influence the morphology, which in turn gives rise to different degrees of stability.^[11] Therefore, to investigate the intrinsic stability of new perovskite compositions, it is possible to circumvent the variability of the morphology of thin films by using single crystals. Crystals typically have fewer defects that act as charge traps,^{[12],[13]} and are characterized by long-term stability.^[2]

Here, we propose to select a metal halide perovskite that was previously synthesized in single crystal form to ensure that it is structurally stable and investigate how the material performs in spin-coated thin films.

A tool that can be used to predict a perovskite's stability is the Goldschmidt tolerance factor, which gives criteria for the radii of the ions that can fit in the structure.^[14] For lead-based perovskites, the incorporation of cesium and formamidinium (FA) makes it possible to improve the Goldschmidt tolerance factor compared with a mixed halide perovskite based on the methylammonium (MA) cation, such as $\text{MAPbI}_{3-x}\text{Br}_x$. For example, the compositions $\text{Cs}_{0.15}\text{FA}_{0.85}\text{PbI}_3$, $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{1.8}\text{Br}_{1.2}$, and $\text{Cs}_{0.05}\text{FA}_{0.16}\text{MA}_{0.79}\text{PbI}_{2.49}\text{Br}_{0.51}$ have a better tolerance factor and, therefore, a higher stability.^{[5],[7],[9]} $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{2.49}\text{Br}_{0.51}$ was used in a perovskite–silicon tandem solar cell with a power conversion efficiency of 23.6% and high environmental stability.^[15]

Here, we investigate similar compounds, with composition $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{3-x}\text{Br}_x$ (where x is 0.45 or 0.6), of which the $x = 0.6$ variety was previously synthesized in single crystal form and demonstrated to be stable.^[16] We report the first investigation on the $x = 0.45$ compound, which we anticipated to be similar to the higher bromine content perovskite in terms of

structural stability. Because of the lower bromine ratio, we expected to have a broader absorption range due to a slightly narrower bandgap, which is favorable for multijunction photovoltaic applications.

We find that these compounds are stable both as single crystals and thin films, which allows for a comparison of the photophysical and structural properties in each form. We also observe that there is a difference in phase purity of the spin-coated thin films. The higher bromine content perovskite has traces of the δ -phase of both CsPbI_3 and FAPbI_3 —both non-perovskite phases—as determined by grazing-incidence wide-angle X-ray scattering (GIWAXS), whereas the material with the lower bromine content only has traces of the δ -phase of FAPbI_3 . Time-resolved photoluminescence experiments indicate that the film containing both non-perovskite phases displays lower charge carrier lifetimes. Interestingly, more commonly applied techniques such as confocal laser scanning microscopy (CLSM) and energy-dispersive X-ray spectroscopy (EDX) cannot detect the impurities in our films. Based on all our data, we conclude that the lower bromine content material is the best choice for optoelectronic applications.

3.2 Results and discussion

$\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ was selected for its structural stability, which is due to its favorable Goldschmidt tolerance factor ($t = 0.84$). $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ has a similar tolerance factor; therefore, we expected it also to be stable. The lower bromine content should lead to an absorption onset at longer wavelengths, which is beneficial for the use in multijunction photovoltaic devices. We verified this by measuring the optical properties of both compounds. Figure 3.1a shows the absorbance of both $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ and $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ in spin-coated thin films. The decreased bromide content of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ leads to a redshift of about 20 nm. This is in agreement with previous literature, where higher bromide content leads to a wider bandgap material.^[16] The photoluminescence (PL) spectra also show a redshift for the sample with the lower bromide content. Here, the shift between the two compositions is smaller (15 nm) compared with that for the absorbance spectra.

During the previously reported synthesis of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{3-x}\text{Br}_x$ perovskites, impurities such as the non-perovskite δ -phases of FAPbI_3 and CsPbI_3 were found.^[16] To verify that the compositions of our films are phase pure, X-ray diffraction (XRD) measurements were performed. Powder XRD measurements were unable to determine the crystal structures of the films: first, the peak intensities cannot be quantitatively analyzed due to the small sample volume probed in this geometry, and, second, the peaks are significantly broader than the instrumental resolution, preventing the resolution of any peak splitting due to tetragonal distortion and making it difficult to detect any compositional inhomogeneity. Nonetheless, a weak unindexed peak at $2\theta = 11.7^\circ$ in both patterns (Figure 3.2), which

3.2. RESULTS AND DISCUSSION

corresponds to the (100) peak of the non-perovskite δ -FAPbI₃ phase (concentration around 1 wt%), is revealed.^[5] However, no traces of δ -CsPbI₃ could be detected with powder XRD.

CLSM was used to verify that the films are free of δ -CsPbI₃. Because the non-perovskite phase of CsPbI₃ has broad photoluminescence ranging from 450 to 600 nm,^[17] it will be discernable from the emission of the cesium-FA compounds. CLSM was performed to check the uniformity of the emission in terms of energy and intensity over the surface of the thin films (Figure 3.4a,b). Because of the band pass filters used in the confocal setup, it is not possible to locate different compositions with only slight variations in the stoichiometry. However, the filter with a band pass of 590 ± 40 nm would be able to detect δ -CsPbI₃. From the photoluminescence maps, there are no traces of emission from δ -CsPbI₃; we only see the emission of the films in the 780 nm long-pass range. In addition, we looked for variations in emission intensity, which might indicate the presence of different phases that act as recombination sites. Both films have good uniformity in the photoluminescence signal, and the only variations arise from morphological features. The morphology was characterized using atomic force microscopy; images of the films are shown in Figure 3.4c–f. The films seem smooth with crystal grain sizes on the order of hundreds of nanometers: this is due to the high number of nucleation sites induced by the antisolvent method during spin-coating.

The structure of the thin films was further studied by GIWAXS (see Figure 3.5a–d for 2D images). The GIWAXS patterns suggest that both thin films have an almost isotropic structure with only a weak orientation of the crystallites. Comparing the integrated intensity versus q plots in Figure 3.5e of Cs_{0.1}FA_{0.9}PbI_{2.55}Br_{0.45} and Cs_{0.1}FA_{0.9}PbI_{2.4}Br_{0.6}, we can see

Figure 3.1: a) Normalized absorbance spectra of spin-coated thin film perovskites with compositions Cs_{0.1}FA_{0.9}PbI_{2.55}Br_{0.45} (black lines) and Cs_{0.1}FA_{0.9}PbI_{2.4}Br_{0.6} (red lines). The inset shows the absorbance over a longer range. b) Normalized photoluminescence spectra of the thin films with the same compositions as in part (a).

Figure 3.2: Powder XRD patterns of thin film samples of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ and $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$. The green triangle indicates the presence of non-perovskite $\delta\text{-FAPbI}_3$ at $2\theta = 11.7^\circ$. Both patterns are offset to aid the visibility of the small peak.

that there are two additional peaks at low q values for the latter material: at $q = 0.69 \text{ \AA}^{-1}$ and $q = 0.82 \text{ \AA}^{-1}$. These q values translate to 2θ angles of 9.7° and 11.5° , respectively. These peaks in the film with higher bromine content are attributed to two nonperovskite phases: the orthorhombic δ -phase of CsPbI_3 and the δ -phase of FAPbI_3 .^{[5],[18]} These phases are present throughout the entire thickness of the $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ film, as shown by the presence of these peaks independently of the incident angle used to acquire the GIWAXS profiles (Figure 3.3). Upon close inspection, we can also find the $q = 0.82 \text{ \AA}^{-1}$ peak in the film of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$, confirming the results obtained with XRD that both films contain the δ -phase of FAPbI_3 . However, no trace of the non-perovskite CsPbI_3 was found. Thus, $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ seems to be less stable than $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ because it forms two different phases which do not contribute to the photocurrent in solar cells. The effect of these two unwanted phases on the charge carrier lifetimes was investigated with time-resolved photoluminescence experiments (Figure 3.5f). We find that the charge carrier lifetimes of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ are much lower than those of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$, and we propose that the δ -phase of CsPbI_3 plays a decisive role here. Combining the longer charge carrier lifetimes, the higher crystalline quality, and the lower bandgap of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$, we can conclude that this is the most promising material for the use in optoelectronic devices.

Figure 3.3: GIWAXS integrated intensity plotted versus q (normalized at $q = 1.4 \text{ \AA}^{-1}$) for the thin films consisting of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ (a) and $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ (b). The incident angles are 0.4° (black), 0.7° (red), 1.5° (blue) and 2.2° (green). These angles correspond to penetration depths of around 50, 120, 270 and 390 nm, respectively. It is clear that the structure of both films does not change throughout the thickness of the layer due to the fixed peak positions. Intensity variations are attributed to variations in the amount of material present at every depth.

Figure 3.4: CLSM false-color images of thin films of a) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ and b) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$. The photoluminescence signal in red is emitting within a 780 nm long-pass filter. Atomic force microscopy images of the morphology of thin films of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ are shown in parts c) and e), and $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ in parts d) and f). The root mean square roughnesses calculated from these figures are 24, 26, 29, and 23 nm, respectively (continued on next page).

Figure 3.4: (continued from previous page) Atomic force microscopy images of e) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ and f) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ thin films.

EDX was used in an attempt to locate the two non-perovskite phases ($\delta\text{-FAPbI}_3$ and $\delta\text{-CsPbI}_3$) in the two films. This technique can be used to observe the spatial distribution of elements and has been used in previous studies on metal halide perovskites to study phase segregation. Examples are element maps of halogen atoms and of various inorganic atoms that are used in hybrid perovskite research.^{[19],[20]} The element maps of the spin-coated layers of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ and $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ obtained through EDX lack order in the distribution of iodine, cesium, bromine, and lead. We conclude that there is no sign of phase segregation at the experimental resolution, which gives an upper limit to the domain size of the impurities of 50 nm. From the full width at half maximum (FWHM) of the fitted peaks in the GIWAXS data, we can extract an estimation of the average domain size for these impurities (the reader is referred to the original publication for details on the GIWAXS fitting and EDX data). Using the Debye–Scherrer equation^[21] under the assumption that the domains are spherical, we obtain average domain sizes for $\delta\text{-CsPbI}_3$ and $\delta\text{-FAPbI}_3$ of 10–15 nm in diameter in the case of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$. More accurate results might be obtained by characterizing the samples with transmission electron microscopy,^[22] however, this is a rather challenging task for this class of materials.

Figure 3.5: GIWAXS patterns of a) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ measured at $\alpha_i = 0.4^\circ$; b) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ measured at $\alpha_i = 0.4^\circ$; c) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ measured at $\alpha_i = 2.1^\circ$; and d) $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ measured at $\alpha_i = 2.1^\circ$ (continued on next page).

Figure 3.5: (continued from previous page) e) GIXWAXS integrated intensity plotted versus q (normalized at $q = 1.4 \text{ \AA}^{-1}$) for the thin films of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{Pb}_{12.55}\text{Br}_{0.45}$ (black) and $\text{Cs}_{0.1}\text{FA}_{0.9}\text{Pb}_{12.4}\text{Br}_{0.6}$ (red). The incident angle was 0.7° , corresponding to a penetration depth of approximately 120 nm. The green triangles indicate the phases found only in $\text{Cs}_{0.1}\text{FA}_{0.9}\text{Pb}_{12.4}\text{Br}_{0.6}$. f) Time-resolved photoluminescence decay of both spin-coated films. The normalized data are plotted on a semilogarithmic scale. The lifetimes extracted from biexponential decay fits are $\tau_1 = 36.3$ ns and $\tau_2 = 178$ ns for $\text{Cs}_{0.1}\text{FA}_{0.9}\text{Pb}_{12.55}\text{Br}_{0.45}$ and $\tau_1 = 24.6$ ns and $\tau_2 = 116$ ns for $\text{Cs}_{0.1}\text{FA}_{0.9}\text{Pb}_{12.4}\text{Br}_{0.6}$.

Figure 3.6: Characterization of the optical and structural properties of the $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ single crystal. a) Normalized absorbance onset. b) The steady-state and c) time-resolved photoluminescence measurements (normalized data). The steady-state emission is centered around 770 nm, with a FWHM of 39 nm. The PL decay in part (c) can be adequately described by a three-exponential decay, in which a strong initial decay ($\tau = 16$ ns) is followed by a much slower decay with time constants of $\tau = 30$ and $\tau = 267$ ns. d) The powder XRD pattern of the single crystal.

3.3. CONCLUSIONS

Considering that we deem $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ the most promising material of the family for optoelectronic applications, we wanted to verify our hypothesis that this material is structurally stable when grown as a single crystal. Single crystals were successfully grown according to a previously reported synthesis.^[16] The absorbance onset of this crystal (Figure 3.6a) starts at around 790 nm and is very similar to that of the corresponding thin film (Figure 3.1a). Steady-state photoluminescence is shown in Figure 3.6b; the emission is centered around 770 nm, which is also in accordance with the emission of the film. However, the FWHM of the emission of the crystal is slightly narrower (39 nm) than that of the thin film (51 nm), confirming the lower degree of energetic disorder.^[23] In addition, the charge carrier lifetimes extracted from the long-lived component of the time-resolved photoluminescence data (Figure 3.6c) are longer on average, confirming the better quality of the crystal. The quality of the single crystal is also evident from the powder XRD pattern shown in Figure 3.6d. There are no visible impurities, and the peaks are narrower than for the thin films. The pattern features peak splitting and can be best fitted using a structural model with the tetragonal space group $P4/mbm$, where the refined lattice parameters are $a = b = 8.8738(4)$ Å, $c = 6.2622(4)$ Å. Space group $P4/mbm$ is a subgroup of the ideal cubic perovskite space group $Pm-3m$ and corresponds to the $a^0a^0c^+$ octahedral tilting scheme in the Glazer notation.^[24] The same structure has been reported for both FAPbI_3 ^[25] and FAPbBr_3 .^[26] Fitting of the peak intensities is not perfect and might indicate that a degree of chemical inhomogeneity remains in the crystal.

3.3 Conclusions

We have studied the photophysics and phase stability of $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ and $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ in thin film form. Despite the small difference in stoichiometry, these materials differ fundamentally in terms of phase purity: $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ has a lower crystalline quality when deposited as thin film. By performing GIWAXS experiments, we found that the corresponding thin film has traces of the non-perovskite phases $\delta\text{-CsPbI}_3$ and $\delta\text{-FAPbI}_3$, which form small domains on the nanometer scale. Considering that $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ only has traces of $\delta\text{-FAPbI}_3$, it is likely that the $\delta\text{-CsPbI}_3$ impurities cause the reduced charge carrier lifetime observed in time-resolved PL measurements for the higher bromine content film. We would like to point out that established techniques such as CLSM and EDX were unable to demonstrate the existence of these impurities. We were able to synthesize $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ as high-quality single crystal, indicating that this material is structurally stable. The better material quality and relatively straightforward stoichiometry, combined with the similarity in bandgap to MAPbI_3 , indicate that $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ has good potential for the use in optoelectronic applications.

3.4 Methods

Thin film fabrication

The films were either fabricated on glass or on prepatterned indium tin oxide (ITO)-coated glass substrates, which were ultrasonically cleaned in detergent solution, deionized water, acetone, and isopropanol, sequentially. After drying them in an oven at 140°C for about 10 min, they were treated with ultraviolet ozone (UV-O₃) plasma for 20 min. The substrates were transferred into a nitrogen-filled glovebox immediately for further processing. Solutions of 1 M Cs_{0.1}FA_{0.9}PbI_{2.55}Br_{0.45} and Cs_{0.1}FA_{0.9}PbI_{2.4}Br_{0.6} were made by dissolving stoichiometric amounts of PbI₂ (TCI Chemicals), PbBr₂ (TCI), formamidinium iodide (FAI) (TCI), and CsI (Alfa Aesar) in a mixture of *N,N*-dimethylformamide (DMF) (Sigma Aldrich) and dimethyl sulfoxide (DMSO) (Alfa Aesar) (4:1 v/v). Solutions were stirred overnight at room temperature before spin coating. Spin coating consisted of a first step at 1000 rpm for 10 s followed by a second step of 4000 rpm for 30 s. Chlorobenzene (Sigma Aldrich) was dropped as antisolvent 5 s prior to the end of the second step. Afterward, the samples were annealed at 100 °C for 10 min. The resulting films had a thickness of around 450–500 nm.

Crystal synthesis

To synthesize Cs_{0.1}FA_{0.9}PbI_{2.55}Br_{0.45}, a 0.8 M solution with respect to [Pb] was prepared. Thus, in 11.25 mL of gamma-butyrolactone (Acros, 99+%), 1.39 g of formamidinium iodide (FAI) (prepared as described in earlier work),^[16] 0.23 g of CsI (ABCR, 99.9%), 3.22 g of PbI₂ (Sigma Aldrich, 99%), and 0.74 g of PbBr₂ (Acros, 98+%) were dissolved, generating a yellow solution. The solution was filtered through a 0.2 µm syringe filter and distributed over three 20 mL vials with a cap. The vessels were next placed in a glycerol bath preheated to 90°C and then heated to 115°C at a rate of 5°C h⁻¹, keeping them at 115°C for an additional 1 h. Next, the crystals were separated from the hot solution, dried with a filter paper, and placed in a desiccator over CaCl₂.

Optical and morphological characterization

Thin film absorption measurements were conducted with a Shimadzu UV-3600 spectrophotometer with an integrating sphere attachment. UV-vis absorbance spectra of the microcrystalline powders were collected using a Jasco V670 spectrophotometer equipped with a halogen lamp and an integrating sphere (ILN-725) with a working wavelength range of 220–2200 nm. Barium sulfate (BaSO₄) was used as a reference for diffuse reflectance. The absorbance spectrum of the single crystal was estimated from reflectance and transmittance spectra collected from a thin layer of crystal that was ground into powder deposited between the glass slides. For the photoluminescence measurements, the second harmonic (400 nm) of a mode-locked Ti:sapphire laser was used as an excitation source. A pulse picker was

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inserted in the optical path to decrease the repetition rate of the laser pulses when needed. The laser power at the sample was adjusted by neutral density filters. The excitation beam was focused with a 150-mm focal length lens, and the fluorescence was collected by the same lens and then coupled into a spectrometer. The spectra were recorded using an Image EM CCD camera (Hamamatsu, Japan). Time-resolved PL spectra were measured using a Hamamatsu streak camera working in single sweep mode. CLSM was performed using an inverted Nikon Ti-eclipse microscope equipped with a Nikon C1 scan head. A CW laser with a wavelength of 488 nm was used as an excitation source and was focused onto the sample using a 40× ELWD objective. The photoluminescence from the sample was collected by raster scanning the excitation beam over the surface and recording the PL at each point using photomultiplier tubes operating in three different wavelength regimes: 515 ± 30 , 590 ± 50 , and 780 nm long-pass. Atomic force microscopy images were acquired with a Bruker Dimension Icon using ScanAsyst mode.

X-ray and structural characterization

XRD was performed under ambient conditions using a Bruker D8 Advance diffractometer in Bragg–Brentano geometry, and operating with a Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$) and a Lynxeye detector. The powder XRD pattern of the crystal was collected in transmission mode (Debye–Scherrer geometry) with a STADI P diffractometer (STOE&Cie GmbH), equipped with a curved Ge (111) monochromator (Cu K $\alpha = 1.54 \text{ \AA}$) and a silicon strip MYTHEN 1K detector (Fa. DECTRIS). For the measurement, the ground crystals were placed between Mylar foils with a small drop of paraffin oil. EDX maps and spectra were obtained using an FEI Nova Nano SEM 650 with an accelerating voltage of 15 kV. The Goldschmidt tolerance factor of the perovskite was calculated according to the ionic radii and formulas as described by Sun et al.^[27] GIWAXS measurements were performed using a MINA X-ray scattering instrument built on a Cu rotating-anode source ($\lambda = 1.5413 \text{ \AA}$). The 2D patterns were collected using a Vantec500 detector (1024×1024 pixel array with pixel size of $136 \times 136 \text{ }\mu\text{m}$) located 93 mm away from the sample. The perovskite films were placed in reflection geometry at certain incident angles α_i with respect to the direct beam using a Huber goniometer. GIWAXS patterns were acquired using a variable incident angle in the range of $0.4\text{--}2.2^\circ$ to probe the thin film structure at an X-ray penetration depth ranging from close to the surface to the entire film thickness. For an ideally flat surface, the value of the X-ray penetration depth (i.e., the depth into the material measured along the surface normal where the intensity of X-rays falls to $1/e$ of its value at the surface) depends on the X-ray energy (wavelength λ), the critical angle of total reflection, α_c , and the incident angle, α_i , and can be estimated using

the relation:

$$\Lambda = \frac{\lambda}{4\pi} \sqrt{\frac{2}{(\alpha_i^2 - \alpha_c^2)^2 + 4\beta^2 - (\alpha_i^2 - \alpha_c^2)}} \quad (3.1)$$

where β is the imaginary part of the complex refractive index of the compound. The direct beam center position on the detector and the sample-to-detector distance were calibrated using the diffraction rings from standard silver behenate and Al_2O_3 powders. All the necessary corrections for the GIWAXS geometry were applied to the raw patterns using the FIT2D and the GIXGUI MATLAB toolbox. The GIWAXS patterns are presented as a function of the horizontal q_y and quasivertical q_z scattering vector as

$$q_y = \frac{2\pi}{\lambda} (\sin(2\theta_f) \cos(\alpha_f)) \quad (3.2)$$

and

$$q_z = \frac{2\pi}{\lambda} (\sin(\alpha_i) + \sin(\alpha_f)) \quad (3.3)$$

where $2\theta_f$ is the scattering angle in the horizontal direction and α_f is the exit angle in the vertical direction. Radial integration of the GIWAXS patterns leads to the integrated intensity $I(q)$ versus q , where q is the modulus of the scattering vector: $q = \frac{4\pi}{\lambda} \sin(\theta)$.

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CHAPTER 4

Photochromism in Ruddlesden–Popper Copper-Based Perovskites: A Light-Induced Change of Coordination Number at the Surface

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Ruddlesden–Popper organic–inorganic hybrid copper-based perovskites have been studied for decades owing to a variety of interesting properties, such as thermochromism and piezochromism, and the mechanisms behind these phenomena have been explained. Another possible property of these materials that has seldomly been investigated is photochromism. This Chapter contains the first report on the photochromic properties of the Ruddlesden–Popper organic–inorganic hybrid copper-based perovskite bis(phenethylammonium) tetrachlorocuprate (also known as phenethylammonium copper chloride). This material has attracted scientific interest owing to the fact that it shows both ferroelectric and ferromagnetic behavior. The work described in this Chapter highlights the difference in stability between two Ruddlesden–Popper copper-based perovskites — with phenethylammonium (PEA) or methylammonium (MA) as the cations — during external stimuli. Various techniques, such as Raman and X-ray photoelectron spectroscopy, and grazing-incidence wide-angle X-ray scattering, combined with optical studies, were used to investigate the underlying photochemical processes at a molecular level. It is found that for the PEA compound, ultraviolet illumination causes a color change from yellow to brown. This is the result of two independent events, namely a Cu^{2+} reduction reaction and a transition from an octahedral copper-chloride structure to square-planar CuCl_4^{2-} . After illumination, the material (brown color) is unstable in air, which is evident from a color change back to yellow. Interestingly, the similar compound bis(methylammonium) tetrachlorocuprate does not display photochromic behavior, which is attributed to the different nature of the two organic cations.

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4.1 Introduction

The family of Ruddlesden–Popper organic–inorganic hybrid perovskites with the structural formula A_2MX_4 — where A is an organic cation with an ammonium group, M a metal anion (e.g., Cu^{2+} , Pb^{2+} , Sn^{2+} , Ge^{2+} , Mn^{2+} , Eu^{2+}) and X a halide anion — encompasses a large selection of materials, each with unique properties.^[1] The halides bind to the metal ions in the form of MX_6 octahedra, which are connected by corner-sharing the four in-plane halide ions.^[2] The organic cations (e.g., methylammonium, butylammonium or phenethylammonium) are located in the voids between the octahedra and interact with them via Coulomb interaction and hydrogen bonding, forming an alternating layered two-dimensional structure.^[1] Depending on the structure of the organic cation, the inorganic octahedral framework might not form. An example is given by the difference in structure between bis(phenethylammonium) tetrabromocuprate, $(C_6H_5C_2H_4NH_3)_2CuBr_4$, and bis[methyl(2-phenethyl)ammonium] tetrabromocuprate, $(C_6H_5C_2H_4NH_2CH_3)_2CuBr_4$. The former adopts the octahedral perovskite structure, but the latter has isolated $CuBr_4^{2-}$ anions; the steric hindrance of the methyl group prevents the formation of a perovskite structure because it hinders the formation of hydrogen bonds. The $CuBr_4^{2-}$ structure allows for more space for the organic cation, thereby enabling hydrogen bonding.^{[2],[3]} Typical geometries for these CuX_4^{2-} ions are square-planar (D_{4h} symmetry) or distorted tetrahedral (D_{2d} symmetry) (see Figure 4.1 for a schematic overview of these geometries).^[4] The difference between these is caused by the strength of the hydrogen bonding of the cation with the halides, where stronger binding leads to a more square-planar character.^[5]

The variety in structures for copper halide phases, combined with the presence of Jahn–Teller effects in these d^9 metal compounds, leads to interesting chemical effects. For instance, the distortion of the CuX_4^{2-} tetrahedral structure and the elongation of certain Cu – X bonds in CuX_6 octahedra can be attributed to the Jahn–Teller effect.^[6] Of particular interest are the copper chloride complexes. These were studied for their piezo- and thermochromism, i.e. the change of color upon pressure and temperature variation, respectively.^{[5],[7]–[15]} Their piezochromism is explained by the tilting of the octahedra and reduction of the Jahn–Teller distortion by compressing the long Cu – Cl bond.^{[7],[8]} Thermochromism often involves the change in coordination geometry from (nearly) square-planar $CuCl_4^{2-}$ at low temperature to a distorted tetrahedron at higher temperatures, due to the decreased strength of the hydrogen bonding.^{[5],[9],[10],[12],[15]} Riley et al. found that the color change in the thermochromic bis(piperazinium) tetrachlorocuprate could also be induced by laser illumination, but could not establish whether this was really caused by photoexcitation (photochromism) or by local heating due to the laser light.^[9]

The work of Pan et al. demonstrated a photochromic effect in $(C_4H_9NH_3)_2CuCl_4$, where a yellow film turned brown after illumination with UV light.^[16] They found little evidence

Figure 4.1: Schematic with examples of the square-planar, distorted tetrahedral and octahedral geometries in top view (top) and side view (bottom). In the case of the distorted tetrahedral geometry the angles between neighboring chloride ions are not necessarily 90° .

4.2. RESULTS

for significant structural changes — infrared spectroscopy indicated a variation in the vibration of the N – H ... Cl bond and the long Cu – Cl bond — and attributed the effect to a change in charge distribution of the dissymmetric Cl – Cu ... Cl bond. In light of the importance of structural changes in the thermochromism described above, we find this conclusion not fully satisfying. In this work we investigated the photochromic properties of a similar material: bis(phenethylammonium) tetrachlorocuprate (also called phenethylammonium copper chloride), or $(\text{PEA})_2\text{CuCl}_4$. This material, which has an octahedral CuCl_6 structure with in-plane Jahn–Teller distortion, displays thermochromism and is a multiferroic due to its coexisting ferromagnetic and ferroelectric order, a property that is highly sought after.^{[14],[17]}

We found that $(\text{PEA})_2\text{CuCl}_4$ changes color upon illumination depending on the atmosphere and the wavelength of the light. Grazing-incidence wide-angle X-ray scattering and Raman spectroscopy revealed that the color change is caused by a structural change in the inorganic framework, which takes place at the surface of the films. Moreover, using X-ray photoelectron spectroscopy we found that the Cu^{2+} at the surface reduces to $\text{Cu}^{0/+}$, which might be explained by the formation of elemental copper in the form of clusters or nanoparticles. Air exposure reverses the color change, which is attributed to the absorption of water, leading to a different structure than the pristine material. The lack of photochromism in the similar compound bis(methylammonium) tetrachlorocuprate (or methylammonium copper chloride) — $(\text{MA})_2\text{CuCl}_4$ — shows that the organic cation plays a decisive role in the process.

4.2 Results

Upon illuminating a yellow film of $(\text{PEA})_2\text{CuCl}_4$ with ultraviolet (UV, $\lambda = 254$ nm) light in nitrogen atmosphere for 45 minutes, the color of the film changes to brown (see Figure 4.2). This color change is evident from the change in absorbance, which can be seen in Figure 4.3a. The pristine material exhibits two absorption peaks in the ultraviolet region, namely the ligand-to-metal charge transfer transitions at 291 and 388 nm, which is characteristic of Jahn–Teller distorted CuCl_4^{2-} compounds.^[18] After exposure to UV light, the intensity of these peaks decreases and both blueshift — to 266 and 385 nm, respectively. Simultaneously, an additional absorption feature forms between 450 and 800 nm. Pan et al. found very similar behavior when they studied the photochromism in the related compound bis(butylammonium) tetrachlorocuprate.^[16] We also studied $(\text{MA})_2\text{CuCl}_4$ under UV illumination and found no color change after 45 minutes of exposure. The absorbance spectra of this film before and after UV-treatment can be seen in Figure 4.3b. Apart from a small deviation in intensity, the two spectra are nearly identical. This result indicates that the organic cation plays an important role in the photochromism of $(\text{PEA})_2\text{CuCl}_4$.

Raman spectroscopy has been used to characterize the vibrational modes of various

Figure 4.2: Photograph of (PEA)₂CuCl₄ (top row) and (MA)₂CuCl₄ (bottom row) thin films. These films are pristine (first column), UV-treated in N₂ (second column) and UV-treated in air (third column). UV treatment was carried out with $\lambda = 254$ nm.

copper chloride complexes.^{[19]–[21]} Our Raman spectrum collected from a single crystal of (PEA)₂CuCl₄ (Figure 4.4) has clear peaks at 179, 247 and 287 cm⁻¹, and is very similar to the low-frequency regime spectrum reported by Caretta et al.^[22] These peaks are all assigned to vibrational modes of Cu – Cl bonds: ν_2 (A_{1g}), ν_4 (B_{2g}) and ν_1 (A_{1g}), respectively.^{[22],[23]} Notably, also prolonged and high intensity exposure to the laser ($\lambda = 532$ nm) of the Raman microscope converts the pristine material into the brown phase (for details, see the supplementary information of the original publication). We attribute this conversion to absorption taking place due to the small — but non-zero — absorption coefficient at this wavelength, combined with the high-power, focused laser light. This is accompanied by the appearance of a dominant peak at 271 cm⁻¹. Increased laser power accelerates the conversion. This behavior is also observed in thin film samples, for which the Raman signal is naturally weaker (see the supplementary material of the publication). Therefore, the color change is not only achieved with UV illumination, but also with focused visible light. Interestingly, the converted brown phase is stable in nitrogen, but not in air. In the latter case the color of the film changes back to yellow (see Figure 4.5) for the absorbance after air exposure), which suggests that the brown phase might be sensitive to oxygen or water. We found that the conversion from the pristine to the brown phase depends on the wavelength and the atmosphere; this is described in the supplementary material of the original publication.

Figure 4.3: Thin film absorbance spectra of a) $(\text{PEA})_2\text{CuCl}_4$ and b) $(\text{MA})_2\text{CuCl}_4$ in the case of a pristine film (black lines) and after 45 minutes of UV illumination in nitrogen environment (red lines). The narrow features between 850 and 900 nm are measurement artifacts.

Figure 4.4: Raman spectra of a pristine $(\text{PEA})_2\text{CuCl}_4$ single crystal (black lines) and of the same crystal after 532 nm laser exposure (red lines). The inset displays a magnification of the low-energy part of the spectra.

Figure 4.5: Thin film absorbance spectra of $(\text{PEA})_2\text{CuCl}_4$ in the case of a pristine film (black line) and after 45 minutes of UV illumination in nitrogen environment (red line). The sample was kept in air for 22 days (blue line), and illuminated with UV for 45 minutes in nitrogen afterwards (green line). The pristine measurement was carried out on a different film to make sure that the material was not in contact with air before UV treatment. The second UV conversion shows the reversibility of the photochromism in $(\text{PEA})_2\text{CuCl}_4$, the spectrum is very similar to that after the first UV treatment (apart from some intensity variations).

4.2. RESULTS

To investigate whether bulk structural changes occur during the conversion, we studied the pristine and converted films of both $(\text{PEA})_2\text{CuCl}_4$ and $(\text{MA})_2\text{CuCl}_4$ using X-ray powder diffraction (XRD). The corresponding diffraction patterns can be found in Figure 4.6; they show the $(00l)$ peaks (only even values of l for $(\text{PEA})_2\text{CuCl}_4$),^{[14],[24]} indicating that the inorganic plane is strongly oriented parallel to the substrate. No discernable new features were detected for the converted $(\text{PEA})_2\text{CuCl}_4$ film compared to the pristine material. The same is true for $(\text{MA})_2\text{CuCl}_4$, as expected since there was no change in the absorbance spectrum after UV treatment.

In our previous work we have demonstrated that XRD is not always the best choice for detailed structural characterization of metal halide perovskites, and we showed that grazing-incidence wide-angle X-ray scattering (GIWAXS) could provide more details.^[25] This is especially true if a texture is present in the perovskite layer.^[26] This advantage is combined with the ability to carry out depth-resolved measurements by varying the incident angle.^{[27],[28]} Figure 4.7 shows the GIWAXS patterns of the pristine and UV-treated $(\text{PEA})_2\text{CuCl}_4$ films at two different incident angles, $\alpha_i = 0.2^\circ$ and 0.8° , which correspond to roughly 25 and 2000 nm of X-ray penetration depth, respectively. The GIWAXS pattern of the pristine material (Figure 4.7a and c) is composed of three strong signals focused along the quasi-vertical q_z direction related to the $(00l)$ reflections, one strong out-of-plane signal (113 reflection) and one weak signal along the q_y direction, related to a $(h00)$ signal. The pattern can be indexed using the known crystallographic structure for $(\text{PEA})_2\text{CuCl}_4$, which is an orthorhombic unit cell of $Pbca$ space group with axes of 7.31 Å, 7.34 Å and 38.64 Å ($a \times b \times c$).^[14] The anisotropic nature of the signals confirms the preferred orientation of the crystallites with the $(00l)$ planes parallel to the substrate (see the supplementary information for more details). The intense $(00l)$ reflections with respect to the much weaker out-of-plane reflections can be explained by a higher degree of ordering of the stacking planes in the vertical z -direction rather than in the xy -plane. This is probably a result of the Jahn–Teller effect in these compounds.

Upon illumination with UV light, the (113) and (200) reflections practically disappear and the $(00l)$ reflections becomes approximately five times weaker, although they do not vanish (see Figure 4.7b and the additional data in the supplementary information of the original publication). This indicates that UV treatment destroys the structural order in the xy -plane and reduces it in the z -direction. This effect is mostly limited to the top part of the film (top hundreds of nm), as the GIWAXS patterns before and after irradiation change negligibly when full X-ray penetration of the film is achieved (Figure 4.7c and d). We also looked at the effect of the color change from brown back to yellow induced by air exposure. After several hours in air, the GIWAXS pattern characteristic of the pristine film is fully recovered (see Figure 4.8).

Figure 4.6: Indexed powder XRD patterns of thin films of a) (PEA)₂CuCl₄ and b) (MA)₂CuCl₄, both pristine and after UV exposure.

Figure 4.7: Wedge corrected GIWAXS patterns for a thin film of $(\text{PEA})_2\text{CuCl}_4$ (a and c) before and (b and d) after UV irradiation measured at two different incident angles ($\alpha_i = 0.2^\circ$ (~ 25 nm) for a and b and $\alpha_i = 0.8^\circ$ (~ 2 μm) for c and d).

Figure 4.8: Evolution of the GIWAXS patterns for the $(\text{PEA})_2\text{CuCl}_4$ film in air a) just after irradiation with UV light, b) 1 hour after irradiation and c) 1 day after irradiation. The incident angle was 0.2° . Note that the sample was kept in the same place during this measurement, to ensure that a quantitative comparison between the different images can be made.

4.2. RESULTS

Figure 4.9: a) XPS spectra of the Cu 2p core level region of a pristine (PEA)₂CuCl₄ film and after exposing it to UV light for various durations. The film was UV-converted *in situ*; XPS spectra were recorded after 45, 90 and 180 minutes. b) Fits of the high-resolution Cu 2p_{3/2} peaks with Cu²⁺ (red curve) and Cu^{0/+} (blue curve) signals for the different data depicted in a).

Due to the conversion taking place mainly at the surface of the thin film, we resorted to X-ray photoelectron spectroscopy (XPS) to study the surface composition of the film. The Cu 2p XPS spectrum of the pristine (PEA)₂CuCl₄ film is shown in Figure 4.9a. The full XPS spectra and the fitted spectra of the other elements are included in the supplementary information of the publication. The film was UV-treated in the XPS setup under vacuum and measured afterwards. The UV-treatment was carried out for a cumulative duration of 45, 90 and 180 minutes. The satellite structures in Figure 4.9a indicate the presence of Cu²⁺ species, as expected.^{[29],[30]} As highlighted in Figure 4.9b, there is an additional feature stemming from Cu^{0/+}, for which the oxidation states cannot be discriminated precisely.^[30] However, it is clear that the ratio of Cu²⁺ to Cu^{0/+} decreases with UV exposure. Initially, Cu²⁺ and Cu^{0/+} make up about 75% and 25% of the Cu 2p_{3/2} signal, respectively, while after 180 minutes of exposure the Cu²⁺ feature represents 43% of the Cu 2p_{3/2} component (Figure 4.10). Additionally, the Cl/Cu atomic ratio decreases from 5.0 in the initial measurement to 2.7 after 180 minutes of UV treatment (see Figure 4.11).

Figure 4.10: Variation of the relative intensities of the two components attributed to Cu^{2+} and $\text{Cu}^{0/+}$ over the course of the UV treatment.

Figure 4.11: Cl/Cu atomic ratio over the course of the UV treatment.

Figure 4.12: Photoluminescence spectra for pristine (black line) and UV-converted (red line) $(\text{PEA})_2\text{CuCl}_4$ films acquired at 5 K. The peak that is marked with an asterisk is a measurement artifact due to stray background light.

We carried out photoluminescence measurements on both the pristine and UV-converted films to see whether the $\text{Cu}^{0/+}$ led to new emission peaks. Laser excitation was performed at 267 nm. The photoluminescence (PL) experiment was carried out at 5 K, a temperature at which the conversion does not take place. Figure 4.12 shows the PL intensity for both pristine and UV-converted $(\text{PEA})_2\text{CuCl}_4$. It is clear that the pristine material does not emit. However, the UV-converted film has a strong signal centered around 550 nm. This is a very valuable finding for identification of the new species that form during the illumination of $(\text{PEA})_2\text{CuCl}_4$.

4.3 Discussion

From XPS we can conclude that UV-treatment of $(\text{PEA})_2\text{CuCl}_4$ results in the reduction of Cu^{2+} to $\text{Cu}^{0/+}$ (Figure 4.9b). The copper reduction during UV irradiation is further confirmed by the decrease in satellite structures (Figure 4.9a). The initial presence of the $\text{Cu}^{0/+}$ component can be assigned to structural defects, partial reduction of Cu on the surface^{[31],[32]} or traces of synthesis precursors.^[31] The decrease in Cl/Cu atomic ratio from 5.0 to 2.7 (Figure 4.11) is a clear indication that copper is in a lower oxidation state. Consequently, the formation of new compounds with Cu in a lower oxidation state has to be taken into consideration. Since the XPS measurement cannot distinguish between the two oxidation states of the $\text{Cu}^{0/+}$ feature, both Cu^+ and elemental copper could be formed in the process. Reports on the photoluminescence of Cu^+ typically show emission with a peak around 515 nm,^{[18],[33]} while copper(I) chloride (CuCl) emits around 390 nm.^[34] Both cannot explain

what we observe in our measurements (550 nm, Figure 4.12). Therefore, we have to look for a different origin. Considering elemental copper, we find that copper nanoparticles (NPs) embedded in a SiO₂ matrix were reported to show photoluminescence around 550 nm, depending on their size.^[35] Such metallic copper NPs have been demonstrated to form through photochemical reduction of Cu⁺ and Cu²⁺, by illuminating precursors — such as CuCl₂ — in solution with UV light.^{[36]–[39]} An example of photoinduced formation of metallic nanoparticles in solid state is the reduction of Au(III) to Au(0) nanoparticles, which occurs when AuCl₄[−] is exposed to UV light.^[40] The presence of copper NPs could also explain the broad feature in the absorbance (Figure 4.3a) between 450 and 800 nm.^[36] Another explanation for the broad absorption is the formation of Cu₂O NPs.^[41] Considering that the conversion takes place in a nitrogen-filled glovebox, we deem the latter improbable.

A partial contribution to the broad absorption feature could also be attributed to the presence of square-planar CuCl₄^{2−} species. The CuCl₄^{2−} ion has a centrosymmetric planar geometry with *D*_{4h} symmetry;^[42] the inorganic plane of (PEA)₂CuCl₄ can be seen as square-planar CuCl₄^{2−} ions linked to form infinite layers — a sort of polymerization — with Cu – Cl – Cu bonds linking the ions.^[4] The absorbance spectrum of square-planar CuCl₄^{2−} displays ligand-field transitions between 500 and 850 nm.^{[20],[43]} The formation of CuCl₄^{2−} can also explain the shift in the UV-region of the absorption spectrum, because these ions have an absorption peak around 267–270 nm, matching perfectly with our spectrum.^{[44],[45]} In addition, the new Raman peak can be attributed to square-planar CuCl₄^{2−}: the totally symmetric stretch of the ion is found at 271 cm^{−1}.^{[20],[46]} Furthermore, there are reports in literature on a thermochromic effect in tetrachlorocuprates(II), where an increase in temperature leads to a (semi)reversible color change from green (square-planar CuCl₄^{2−}) to yellow (CuCl₄^{2−} in the form of a distorted tetrahedron).^{[9],[47]} For bis(piperazinium) tetrachlorocuprate this effect also occurs upon illumination.^[9] In our case, the effect would involve a change from octahedral to square-planar CuCl₄^{2−}, which would mean that the connected square-planar CuCl₄^{2−} ions would become isolated. A similar process has been reported as a thermal effect in a hydrated nickel bromide compound.^[48] It is also important to underline that the transition from octahedral to square-planar CuCl₄^{2−} could explain the disorder in the *xy*-plane, which was demonstrated with GIWAXS (see Figure 4.7b).

The absorbance spectrum of UV-treated (PEA)₂CuCl₄ still shows features from the pristine layer in the form of a shoulder at 291 nm (see Figure 4.3a). This can be explained by the results of the GIWAXS experiment, where we found that the conversion occurs in the first hundreds of nanometers from the surface. Below, in the bulk of the layer, no conversion takes place. This is the result of the limited penetration depth of UV light in our material. Therefore, the light can only convert (PEA)₂CuCl₄ in the first hundreds of nanometers.

4.3. DISCUSSION

Air exposure leads to the color change from brown to yellow. Bhattacharya et al. found that the thermochromic bis(benzimidazolium) tetrachlorocuprate can exist in two forms: the yellow non-hydrated phase and a green hydrated phase.^[11] The former consists of isolated distorted tetrahedral CuCl_4^{2-} ions, the latter has alternating polymeric $[\text{CuCl}_4^{2-}]_\infty$ and $[\text{CuCl}_2(\text{H}_2\text{O})_2]_\infty$ chains.^[49] Upon heating, the green hydrated phase loses the water molecules due to a thermochromic transition. The resulting yellow phase has isolated CuCl_4^{2-} ions. The authors also demonstrated the reverse process, where the non-hydrated compound absorbs water to form the polymeric $[\text{CuCl}_2(\text{H}_2\text{O})_2]_\infty$ chains.^[49] Therefore, their system is a good example of a monomeric – polymeric transformation based on thermochromism and exposure to water molecules. We suppose that the mechanism behind the color change back to yellow in air for our system works in an analogous way, i.e. the square-planar CuCl_4^{2-} ions in the brown phase could change to alternating polymeric $[\text{CuCl}_4^{2-}]_\infty$ and $[\text{CuCl}_2(\text{H}_2\text{O})_2]_\infty$ chains after absorbing water molecules from the air. This would look more similar to the structure of pristine $(\text{PEA})_2\text{CuCl}_4$ and could explain the recovery of the (113) and (200) reflections in the GIWAXS experiment due to the longer structural order of the polymeric chains.

At this point we are left to explain the lack of photochromic behavior in $(\text{MA})_2\text{CuCl}_4$ (see Figure 4.3b). We propose that this is due to a difference in the strength of the hydrogen bonding between the organic cation and the halide ions. Bloomquist et al. studied the thermochromic change of bis(isopropylammonium) tetrachlorocuprate and found that this involves a change from a linear structure of ribbon-like connected square-planar CuCl_4^{2-} to isolated distorted tetrahedral CuCl_4^{2-} .^[10] This is caused by a weakened hydrogen bond between the organic cations and the chloride ions due to an increase in temperature. Without the hydrogen bond there is an excess electrostatic charge on the chloride ions, which leads to a relaxation of the coordination of the copper complex to a distorted tetrahedral structure. The CH_3 -group in MA has an electron donating character, whereas the phenyl ring in PEA is electron withdrawing. This might lead to a difference in hydrogen bonding strength and stability of the octahedral structure. Additionally, methylamine does not absorb 254 nm light, whereas phenethylamine does.^{[50],[51]} This means that only PEA will be in an excited state upon illumination. It has been shown that the most stable conformer of phenethylammonium has a gauche confirmation of the NH_3^+ -group with respect to the alkyl chain, in which one hydrogen atom of the NH_3^+ -group is oriented towards the benzene ring.^[52] In the excited state of this molecule, this hydrogen atom is situated closer to the benzene ring.^[53] Therefore, UV illumination could weaken the hydrogen bonding between PEA and the chloride ions.

4.4 Conclusions

This work is the first report on the photochromic properties of the hybrid organic–inorganic Ruddlesden–Popper perovskite $(\text{PEA})_2\text{CuCl}_4$. Exposure to UV light ($\lambda = 254 \text{ nm}$) in a nitrogen environment leads to a color change of the film from yellow to brown, but the color change can also occur in other conditions (312 nm light in air). This is accompanied by a loss in structural order in the xy -plane of the film’s surface, as determined by GIWAXS. X-ray photoelectron spectroscopy shows that UV illumination causes the reduction of Cu^{2+} to $\text{Cu}^{0/+}$. As a result of the illumination, new features were found in the absorbance and Raman spectra of UV-converted $(\text{PEA})_2\text{CuCl}_4$, which can be explained by the presence of square-planar CuCl_4^{2-} species. The instability of UV-converted $(\text{PEA})_2\text{CuCl}_4$ in air is demonstrated by a color change back to yellow, which is accompanied by a recovery of the structural order, as seen in the GIWAXS pattern. The similar compound $(\text{MA})_2\text{CuCl}_4$ does not show photochromic behavior, which we attribute to a difference in hydrogen bond strength between the organic cation and the chloride anions due to the different chemical nature of the two organic cations.

4.5 Methods

Film processing

Preparing and spin coating the metal halide perovskite solutions took place in a glovebox with nitrogen environment. A solution of $(\text{PEA})_2\text{CuCl}_4$ was made by dissolving phenethylammonium chloride (Sigma Aldrich) and copper(II) chloride (Sigma Aldrich) in *N,N*-dimethylformamide (DMF, Sigma Aldrich) in a 2:1 molar ratio. The final concentration of the solution was 1 M. For $(\text{MA})_2\text{CuCl}_4$, methylammonium chloride (Sigma Aldrich) was used instead. Here, two solvents, DMF and dimethyl sulfoxide (DMSO, Alfa Aesar), were used in a 4:1 v/v ratio to improve the solubility. This solution had a 0.8 M concentration. Solutions were stirred at room temperature overnight before spin coating. The substrates were either made of glass or quartz and were cleaned with detergent solution, and subsequently ultrasonically cleaned in deionized water, acetone and isopropanol. After drying them in an oven at 130 °C for 10 min, they were treated with ultraviolet ozone (UV- O_3) for 20 min. Spin coating involved a rotation of 5000 rpm during 45 seconds for $(\text{PEA})_2\text{CuCl}_4$ and 3000 rpm for $(\text{MA})_2\text{CuCl}_4$. To prevent charging effects in the XPS experiment we made a very thin film (50–150 nm) on a silicon substrate. This was done by blade coating because it offered us better control over the morphology of a very thin film compared to spin coating. For this experiment, the $(\text{PEA})_2\text{CuCl}_4$ solution was diluted to 0.1 M and this was coated at 120 °C with a blade speed of 40 mm s⁻¹.

Crystal synthesis

Single crystals of $(\text{PEA})_2\text{CuCl}_4$ were grown by the slow evaporation of solvent at 60 °C. A 1:2 molar ratio of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma Aldrich; 99.95%) and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2 \cdot \text{HCl}$ (Sigma Aldrich; 98%) were dissolved in absolute ethanol (J.T. Baker) and placed in an oven at 60 °C. After approximately one week, transparent, yellow single crystals had formed. The crystals are shaped as platelets with sizes ranging from 0.1 to around 6 mm.

UV treatment

For the UV treatment the $\lambda = 254$ nm setting of a Spectroline EBF-280C/FE lamp was used. The UV treatment was carried out in a N_2 -filled glovebox for 45 minutes. The distance from the lamp to the sample was approximately 15 mm. For the experiment with the $\lambda = 312$ nm UV source, the longer wavelength setting on the same lamp was used.

Absorbance

The thin film samples for the absorbance measurement were made on quartz, and characterized with a Shimadzu UV-3600 spectrophotometer with an integrating sphere attachment.

X-Ray diffraction

Powder XRD data were collected under ambient conditions using a Bruker D8 Advance diffractometer in Bragg–Brentano geometry and operating with Cu K α radiation ($\lambda = 1.54$ Å). A fixed slit width was used for the incident beam (1 mm) and diffracted beam (3 mm). Samples were rotated at 60 revolutions per minute. The angle 2θ was scanned between 5 and 40 degrees using a 0.015 degrees step size.

Grazing-incidence wide-angle X-ray scattering

GIWAXS experiments were performed at the Multipurpose Instrument for Nanostructured Analysis (MINA) at RUG. The instrument is equipped with a rotating Cu anode source ($\lambda = 0.15413$ nm). GIWAXS patterns were acquired using a Pilatus 300 K solid state detector from Dectris with pixel size 0.172 mm $\times$ 0.172 mm. The sample alignment and the incident angle setting were achieved using motorized Huber positioning stages. The sample-to-detector distance (S-to-D) and the position of the direct beam on the detector were calibrated using known diffraction peaks from a silver behenate standard sample. The calibrated S-to-D value was 90 mm. The missing wedge correction and the intensity line cuts were obtained using the GIXGUI software.^[54] In the case of an ideally flat surface, the X-ray penetration depth (i.e. the depth into the material measured along the surface normal where the intensity of X-rays falls to $1/e$ of its value at the surface) depends on the wavelength λ of the X-rays, the critical angle of total reflection, α_c , and the incident angle, α_i , and can be estimated using the relation:

$$\Lambda = \frac{\lambda}{4\pi} \sqrt{\frac{2}{(\alpha_i^2 - \alpha_c^2)^2 + 4\beta^2 - (\alpha_i^2 - \alpha_c^2)}}, \quad (4.1)$$

where β is the imaginary part of the complex refractive index of the compound.

X-ray photoelectron spectroscopy

XPS was performed using a Surface Science SSX-100 ESCA instrument with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV). The pressure in the measurement chamber was maintained below 1×10^{-9} mbar during data acquisition. The electron take-off angle with respect to the surface normal was 37°. The XPS data were acquired by using a spot size of 1000 μ m diameter and the energy resolution was set to 1.3 eV for both the survey spectra and the detailed spectra of the C 1s, Cl 2p, Cu 2p, N 1s and O 1s core level regions. Furthermore, a gold mesh placed 1 mm above the sample was used during the XPS measurements in order to prevent the charging effect. Binding energies are reported ± 0.1 eV and referenced to the C 1s photoemission peak centered at a binding energy of 284.8 eV.^[55] All XPS spectra were analyzed using the least-squares curve fitting program Winspec (LISE laboratory, University of

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Namur, Belgium). Deconvolution of the spectra included a Shirley^[56] baseline subtraction and fitting with a minimum number of peaks consistent with the structure of the components of the thin film, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. The uncertainty in the peak intensity determination is within 2% for all core levels reported. All measurements were carried out on freshly prepared samples. Exposure to UV (254 nm) light was conducted *in situ* through a special window of the vacuum chamber.

Raman spectroscopy

Raman spectroscopy was carried out using a confocal inVia Qontor micro-Raman setup from Renishaw. Excitation occurred at 532 nm through a 50× objective, with a power between 39.5 and 73.4 μ W. The light was collected in backscattering geometry, dispersed with a 2400 lines per millimeter grating and detected with a silicon CCD. Spectral calibration was assured through a silicon reference.

Photoluminescence spectroscopy

For low-temperature photoluminescence spectroscopy, thin films were mounted into a cryostat (Oxford Instruments Optistat CF) in an inert atmosphere. The samples were excited at 4.6 eV (267 nm) using the third harmonic of a mode-locked Ti:sapphire laser (Mira 900, Coherent) operating at a repetition rate of 76 MHz. The excitation beam was spatially limited by an iris and focused onto the sample using a 150 mm focal length lens in a reflection geometry. The pump fluence was controlled using an adjustable neutral density filter. The photoluminescence was collected into a spectrometer and recorded by an ImagEM CCD camera (Hamamatsu, Japan).

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CHAPTER 5

Detecting Alcohol Vapors Using Two-Dimensional Copper-Based Ruddlesden–Popper Perovskites

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The detection of alcohol vapors has many important applications, such as measuring the breath ethanol content to prevent drug-impaired driving. A medical application is the detection of 1-propanol because this compound was found to be a potential marker for lung cancer screening. In this Chapter we report an alcohol sensor using the two-dimensional Ruddlesden–Popper perovskite bis(phenethylammonium) tetrachlorocuprate — $(\text{PEA})_2\text{CuCl}_4$, also known as phenethylammonium copper chloride — as the sensing material. The device is based on a change in conductance upon exposure to alcohol vapors. A comparison between pristine $(\text{PEA})_2\text{CuCl}_4$ and $(\text{PEA})_2\text{CuCl}_4$ after a treatment with ultraviolet light shows that the latter has a higher conductance. Devices made with this UV-converted material show a strong response to 1-propanol vapors, starting from a concentration around 2000 parts per million (ppm). Additionally, these devices demonstrate stable behavior in a nitrogen atmosphere. During the stabilization of the 1-propanol flow rate, the concentration fluctuates. These fluctuations were detected by monitoring the current of the device over time, down to steps in 100 ppm around a concentration of 8000 ppm. The conductance of the devices decreases in contact with air. However, this process can be reversed by additional ultraviolet illumination, thereby making the devices reusable.

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5.1 Introduction

One of the strengths of hybrid inorganic–organic metal halide perovskites is their versatility, which is evident from the various types of devices that were made with this class of materials. Besides the predominant application in thin film solar cells,^{[1]–[5]} there have been reports on other devices such as photodetectors, lasers, and light emitting diodes.^{[6]–[11]} The focus on optoelectronic applications does not do the unique character of metal halide perovskites justice because their tunable composition and excellent electronic properties enable their use in many more fields of research.^{[3],[5],[12]} Examples of these underrepresented, yet technologically relevant devices are gas sensors. Only a small number of these devices were reported in the literature. Maity et al. demonstrated an ammonia sensor based on methylammonium lead iodide,^[13] and Li et al. used methylammonium lead bromide to detect the same compound.^[14] Zhu et al. were able to detect p-xylene in the parts per million (ppm) range using $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$.^[15]

The capability of methylammonium lead bromide (MAPbBr_3) to detect gases, such as oxygen and water vapor, was demonstrated by our group.^[16] It was found that the photoluminescence intensity of a MAPbBr_3 single crystal kept in air is higher than that in vacuum and a nitrogen atmosphere. This was explained by the physisorption of oxygen onto the crystal surface, where the O_2 molecules passivate surface trap states. The nature of these trap states and the passivation mechanism were recently revealed through calculations based on density functional theory, demonstrating that bromide vacancies can generate localized charge traps on the MAPbBr_3 surface.^[17] Restoring the fully delocalized charge density can take place through passivation of the undercoordinated lead atom by hydroxyl (OH^-) groups.

Another well-known type of chemical compound containing hydroxyl groups is the alcohol. Two types of alcohols that play very important roles in society and healthcare are ethanol and 1-propanol. The detection of these alcohols is crucial: ethanol is a cause of drug-impaired driving and 1-propanol is found in the breath of lung cancer patients and is seen as a potential marker for lung cancer screening.^[18] There are a number of papers describing sensors that can detect these two alcohols, but these are often based on complicated mechanisms. Examples are sensors based on oxides, whose conductance changes are based on adsorption of the gas; these devices typically operate at high temperature (130–400 °C).^{[19]–[22]} Other sensors have working mechanisms based on arrays of micromechanical cantilevers,^[23] changes in the refractive index^[24] or the emission wavelength,^[25] or use materials which require a lot of energy for their fabrication such as single-walled carbon nanotubes.^[26] The importance of the aforementioned applications justifies the need for a portable alcohol sensor without a complex working mechanism.

Our previous work on MAPbBr_3 gas sensors demonstrated that a perovskite single crystal with two metal contacts can be used to sense oxygen through changes in its conductance,

without needing high temperature.^[16] We hypothesized that such a simple device architecture might also be promising for the detection of alcohol vapors. We looked into alternative perovskites due to the response of methylammonium lead bromide to oxygen and water, which would not make for reliable sensors under ambient conditions. Since stability in air is often low for three-dimensional lead- and tin-based halide perovskites,^{[27],[28]} we turned our attention to the two-dimensional copper-based Ruddlesden–Popper perovskite bis(phenethylammonium) tetrachlorocuprate (also known as phenethylammonium copper chloride), $(\text{PEA})_2\text{CuCl}_4$. The reason for selecting a copper-based perovskite is to prevent the use of lead and tin, which can be harmful to the environment and human life.^[29]

$(\text{PEA})_2\text{CuCl}_4$ is an air-stable ferromagnetic insulator (at temperatures below 13 K),^[30] whose surface conductivity can be increased by covering it with an organic electron donor.^[31] Arkenbout et al. found that $(\text{PEA})_2\text{CuCl}_4$ has a low conductivity and attributed this to two factors; the first is the ionic character of the bonds between copper and chloride, which leads to localized charge carriers. The second factor is the Jahn–Teller effect occurring in Cu^{2+} compounds, which leads to an antiferrodistortive ordering of the orbitals of the copper ions.^[31] Our recent publication on $(\text{PEA})_2\text{CuCl}_4$ demonstrated that this material exhibits photochromism, i.e., it changes from a yellow to a brown phase upon exposure to ultraviolet (UV) light (see Chapter 4).^[32] During this process, the octahedral copper-chloride structure at the surface changes to isolated square-planar CuCl_4^{2-} ions, destroying the structural order in the inorganic xy -plane. In this work, we compare both phases of $(\text{PEA})_2\text{CuCl}_4$, with the goal of using these materials for vapor sensing applications. For both phases, the conductance of the devices is on the order of picosiemens in an inert atmosphere (N_2). Devices with UV-converted $(\text{PEA})_2\text{CuCl}_4$ have a higher conductance on average, which makes them more resilient to measurement errors. We find that exposure to 1-propanol vapor significantly improves the conductance of the material in the brown UV-converted $(\text{PEA})_2\text{CuCl}_4$. Fluctuations in the 1-propanol concentration on the order of 100 parts per million were detected, making UV-converted $(\text{PEA})_2\text{CuCl}_4$ a very promising compound for use in 1-propanol vapor sensors. Despite the stability in air of pristine $(\text{PEA})_2\text{CuCl}_4$, the brown phase is not stable in air, which is evident from a decrease in conductance. However, the conductance can be increased again by illuminating the device with UV light; the regeneration of the devices makes them reusable.

5.2 Results and discussion

Fabrication of the $(\text{PEA})_2\text{CuCl}_4$ film (see Figure 5.1a for the crystal structure of the pristine material) was based on the spin coating technique, which leads to a strong parallel orientation of the inorganic planes with respect to the substrate.^[32] This orientation is favorable for conduction in two-dimensional hybrid perovskites when a planar device geometry is

Figure 5.1: a) The crystal structure of pristine (PEA)₂CuCl₄ as determined by Caretta et al.,^[34] visualized using Mercury.^[35] A schematic diagram of the (PEA)₂CuCl₄ alcohol vapor sensor in b) inert atmosphere and c) in the presence of 1-propanol vapor.

used.^[33] Devices were fabricated by evaporating 80 nanometer interdigitated gold contacts with a 200 μm channel in-between (see Figure 5.1b for a device schematic and the supplementary material of the original publication for a microscope image of the interdigitated contacts). By applying a bias across the device, we can measure the current flowing through the surface plane, which we can alter by exposing the device to alcohol vapors (Figure 5.1c). From the current–voltage ($I - V$) curves, we extracted the conductance of our devices.

First, we compared the conductance of pristine and UV-converted (PEA)₂CuCl₄ devices in nitrogen without any alcohol present. We found that the average conductance of a device made with a pristine film is 5.4×10^{-13} S (see the supplementary material of the original publication for an overview of the data). The mean conductance of the UV-converted devices is 1.2×10^{-12} S, two times higher than that of the pristine devices. A possible explanation for this behavior is that the charge carrier blockade caused by the antiferrodistortive orbital ordering — a characteristic of the pristine material^[31] — is removed by the structural change from an octahedral copper chloride structure to square-planar CuCl₄²⁻ ions upon UV exposure.^[32] This would lead to a higher conductance, analogous to the findings of Arkenbout et al.^[31] For both the pristine and UV-converted material, our conductance varied from device to device. We attributed this to slight variations in perovskite film morphology due

Figure 5.2: The conductance of a UV-converted $(\text{PEA})_2\text{CuCl}_4$ device in nitrogen over time.

to the spin coating technique used to fabricate the layer, which could also affect the quality of the gold contacts. However, the lower conductance of the pristine material is undesirable since it approaches the detection limit of our experimental setup, making the measurements with these devices more prone to errors. Therefore, we focused our experiments on the UV-converted devices.

As mentioned, the low currents observed in the measurements are sensitive to noise. It is important that a sensor displays stable values under steady-state conditions to ensure reliable operation. We tested the stability of our device by measuring the conductance in nitrogen over time; the results are shown in Figure 5.2. This device has an initial conductance of 1.1×10^{-12} S, which is relatively constant over time, showing that the device has a stable baseline.

With the nitrogen measurements in mind, we look at the response of the device to alcohol vapor. We mix anhydrous alcohol with nitrogen using a custom-made setup (see Figure 5.9 in Section 5.4), where we can control the flow rate of both the alcohol and the gas into a mixer device. The resulting mixture is led into the chamber with the sample. By controlling the flow rate of the alcohol, we can expose our device to various concentrations of the alcohol. First, we checked whether our setup without a $(\text{PEA})_2\text{CuCl}_4$ device is affected by the presence of alcohol vapors. We made reference devices consisting of gold electrodes deposited directly on glass and exposed them to various concentrations of 1-propanol (1-PrOH). The response in terms of conductance vs concentration is shown in Figure 5.3, along with an average response of the three reference devices. It is clear that increasing the 1-PrOH concentration leads to a significant improvement in conductance for our reference, and therefore, we corrected the data of our actual $(\text{PEA})_2\text{CuCl}_4$ devices for this effect. This

Figure 5.3: Conductance of glass reference devices for various concentrations of 1-PrOH in nitrogen environment (depicted as circles and triangles). The average response of the three devices is shown as the black squares.

increase in conductivity might be explained by adsorption of 1-propanol at the surface of the glass between the gold electrodes. Voorthuyzen et al. found an increase in surface conductivity of silicon dioxide after exposure to humid air.^[36] They attributed this to physisorption of water vapor.

The response of a UV-converted $(\text{PEA})_2\text{CuCl}_4$ device to various concentrations of 1-PrOH was measured, after which we subtracted the conductance of the reference devices. Here, the response (R) is defined as the ratio of the conductance in 1-PrOH (σ_V) and N_2 (σ_N): $R = \sigma_V/\sigma_N$. Figure 5.4 shows the response of the best performing device. It is clear that the conductance of the UV-converted $(\text{PEA})_2\text{CuCl}_4$ improves with the increasing 1-propanol concentration. After correction for the glass reference device, we observe a 37-fold increase in conductance at around 10000 ppm. At lower concentrations, the improvement is also visible (see the supplementary material of the original publication for a closer look at this regime). However, due to the low currents, the device is still affected by small fluctuations, which prevents us from discerning a clear response until 2000–3000 ppm, after which the effect becomes very pronounced. The responses from additional devices with UV-treated $(\text{PEA})_2\text{CuCl}_4$ are shown in Figure 5.5 (for a closer look at the response at low concentration, see the supplementary material of the original publication). Although there is some variation in the response between devices, we see that they are all capable of detecting 1-propanol. Like the variation in σ_N , we attribute this to differences in device quality, and we believe that with proper control over the film formation, we can reach both better sensitivity and reproducibility.

Figure 5.4: Response of the best performing UV-converted $(\text{PEA})_2\text{CuCl}_4$ vapor sensor to varying concentrations of 1-PrOH in the nitrogen environment, plotted on a semi-logarithmic scale.

Figure 5.5: Responses of six UV-converted $(\text{PEA})_2\text{CuCl}_4$ devices to 1-PrOH, plotted in semi-logarithmic scale. The green diamonds lack some data points, which is due to the fact that the conductance there was lower than that of the glass reference. Therefore, these points were taken out of consideration.

5.2. RESULTS AND DISCUSSION

Figure 5.6: Fluctuation in the concentration of 1-PrOH in the alcohol/nitrogen mixture over time (top) and the resulting signal in the form of current (at 10 V bias) in a UV-converted $(\text{PEA})_2\text{CuCl}_4$ device (bottom). This fluctuation in the concentration is a result of the stabilization of the flow rates of 1-PrOH and N_2 , and the 1-PrOH concentration is an approximation based on these flow rates.

An important aspect of vapor sensors is that the devices should sense a variation in the concentration quickly. Although we could not accurately measure the rise time due to the limitations of the setup, we did investigate the sensitivity of the sensor to variations in the alcohol concentration over a longer time scale. Figure 5.6 shows the time evolution of both the concentration of 1-PrOH in the alcohol/nitrogen mixture and the current of a device biased at 10 V. The concentration fluctuates around 8000 ppm, a region where we see a relatively strong response, which allows us to measure these fluctuations in the concentration reliably. The resemblance between the two signals is very strong, indicating that our setup accurately measures these fluctuations, even the ones on the order of 100 ppm.

The sensitivity S — at a concentration around 8000 ppm — can be approximated by the difference in current (ΔI) for each fluctuation in the concentration (ΔC): $S = \Delta I / \Delta C$. Looking at the difference between peaks and subsequent valleys in the signals (and excluding the peak around 10 s for the lack of a clear signals), we find that the device has an average sensitivity of 0.14 pA/ppm. Additionally, the response seems to be very fast. This indicates the potential of these devices for vapor detection applications.

Figure 5.7: Response of a UV-converted $(\text{PEA})_2\text{CuCl}_4$ vapor sensor to varying concentrations of EtOH in nitrogen environment.

After detecting 1-PrOH, we tested whether UV-converted $(\text{PEA})_2\text{CuCl}_4$ is capable of detecting ethanol (EtOH) too. The reference measurement described above was also carried out for EtOH (one device, see the supplementary material of the publication), and the response of the actual device was corrected for this, as for 1-PrOH. Three devices were characterized, and surprisingly, the response to EtOH is very different from that to 1-PrOH. If there is any response at all, it is much weaker, as can be seen from the best performing device in Figure 5.7. The response fluctuates between 1 and 1.3 over the entire range (0 to about 12000 ppm), with some outliers in the data points. There might be an underlying trend, but the response is not as clear as for 1-PrOH. Based on the available data, we cannot conclude whether UV-converted $(\text{PEA})_2\text{CuCl}_4$ can detect ethanol vapor. The reason for the difference in response to the two alcohols is still under investigation. However, our data indicate that UV-converted $(\text{PEA})_2\text{CuCl}_4$ is a promising material for the detection of 1-PrOH.

Finally, we tested the stability of our devices over time and in air. We compared the initial conductance of a device with the conductance 3 months later. Both measurements were carried out in nitrogen, and the device was also kept in nitrogen between the measurements. However, the device was transported through air, and the contacts with the gold electrodes (made with silver paste) had to be reapplied after 3 months. Figure 5.8 shows that the conductance of the device after 3 months is much lower (8.2×10^{-13} S) than the initial conductance (2×10^{-12} S). This value remains quite constant over the course of 30 min. After that, the sample holder was evacuated and refilled with ambient air. This resulted in a drop of the conductance over 30 minutes to 6.4×10^{-13} S. Considering that UV-converted $(\text{PEA})_2\text{CuCl}_4$ is not stable in air,^[32] this degradation in conductance is not unexpected. After

5.3. CONCLUSIONS

Figure 5.8: Conductance of a UV-converted $(\text{PEA})_2\text{CuCl}_4$ vapor sensor over time. The blue triangle depicts the initial average conductance in nitrogen. The measurements depicted in the blue frame were acquired after 3 months of storage in nitrogen. Here, the black squares depict measurements in nitrogen, and the red circles are air measurements. After the air exposure, the device was brought into a nitrogen-filled glovebox and illuminated with 254 nm light for 45 min. The subsequent measurements in nitrogen and air are shown in the green frame.

the air exposure, the sample was illuminated with UV light for 45 minutes in a nitrogen-filled glovebox. This led to an increase in the conductance in nitrogen to 1.54×10^{-12} S. Therefore, the UV treatment recovered the conductance significantly. Until the device was exposed to air again, this value was fairly stable. However, upon air exposure, the conductance drops considerably over the course of 10 minutes. After that, it seems to stabilize around 9.2×10^{-13} S. From this experiment, we conclude that the conductance of our sensor can degrade over time (e.g., in air), a process that is reversible by UV treatment in nitrogen.

5.3 Conclusions

We have made a $(\text{PEA})_2\text{CuCl}_4$ -based alcohol vapor sensor, by using the brown UV-converted $(\text{PEA})_2\text{CuCl}_4$ as the sensor material. This UV-converted phase has a higher conductance than pristine $(\text{PEA})_2\text{CuCl}_4$, making it more resilient to fluctuations in current. Our best performing device has a response R of 37 at 10000 ppm and could detect 1-propanol concentrations in nitrogen down to 2000–3000 ppm. Although quantitative measurements could not be made, it is clear that the response of the sensor to fluctuations in the 1-PrOH concentration is fast. Moreover, fluctuations in the concentration on the order of 100 ppm could be detected at high concentrations (around 8000 ppm). The devices are stable in nitrogen,

but their conductance decreases in air. Subsequent UV treatment in nitrogen leads to a recovery of the conductance, thereby making the devices reusable. Our results show that UV-converted $(\text{PEA})_2\text{CuCl}_4$ has great potential as material to sense 1-PrOH vapor. Interestingly, with the current data, we cannot conclude whether the device can detect ethanol vapor due to the lack of a strong response in our experiments. Future research is needed to explain the mechanism behind the response to 1-PrOH and to improve the conductance of the devices to make the output more resilient to fluctuations in current and, therefore, more sensitive to lower concentrations. Additionally, more elaborate device architectures might help improve the sensitivity of the devices.

5.4 Methods

Device fabrication

The $(\text{PEA})_2\text{CuCl}_4$ solution was prepared and spin coated in a nitrogen-filled glovebox. The solution was made by dissolving phenethylammonium chloride (Sigma Aldrich) and copper(II) chloride (Sigma Aldrich) in *N,N*-dimethylformamide (Sigma Aldrich) in a 2:1 molar ratio. The final concentration of the solution was 1 M. The solution was stirred over night at room temperature. Glass was used as a substrate for the spin coated films; this was cleaned with detergent solution, followed by ultrasonic baths in deionized water, acetone and isopropanol. Spin coating consisted of one step at 5000 rpm, with an acceleration of 2000 rpm/s for 45 seconds. Subsequently, UV treatment was carried out in the glovebox for 45 minutes with the $\lambda = 254$ nm setting of a Spectroline EBF-280C/FE lamp in case a brown phase was desired. To complete the device, 80 nm gold contacts were evaporated by using a mask with interdigitated electrodes, creating a total working area of approximately 48 mm^2 . Silver paste was used to connect these electrodes to carry out electrical characterization.

Fluid mixing setup

A custom-made fluid mixing setup was used to control the concentration of alcohol in carrier gas (N_2). We used a Bronkhorst MINI CORI-FLOW M12 to regulate the flow rate of alcohol. The flow of N_2 was controlled by a Bronkhorst EL-FLOW SELECT F-201CV. The two fluids were mixed by a Bronkhorst CEM EVAPORATOR W-102A operating at 40°C and the resulting mixture was fed into a custom-made sample chamber. A vacuum pump was used to ensure flow through the sample chamber. Nitrogen (Linde) was $\geq 99.999\%$ pure, and the alcohol used was anhydrous (Acros, 99.5% purity). FLUIDAT, an online flow calculation tool, was used to determine the alcohol concentration in N_2 .

Electrical characterization

Keysight B2912A Precision Source/Measure Unit was used for electrical characterization. For the $I - V$ measurements the bias on the device was swept from -10 to 10 V and back in steps of 200 mV, while measuring the current. The signal was averaged over 20 power line cycles for higher accuracy. The conductance was extracted from the slopes of the $I - V$ curves for both the forward and reverse scan. Two scans were performed at each alcohol concentration, giving four values for the conductance at each point; the average value was used for the data processing. The $I - t$ measurements were carried out with 10 V bias; the current was measured every 100 ms.

Figure 5.9: Schematic of the fluid mixing setup.

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Summary

Hybrid organic-inorganic metal halide perovskites form a versatile group in the class of organic-inorganic hybrid materials. This is exemplified by the diversity in devices that make use of these perovskites, such as solar cells, light emitting diodes, lasers and gas sensors. This range of applications is made possible by the ability to tune the optical, electrical and other physical properties of a perovskite by changing its chemical composition. For instance, by replacing iodide with bromide in the commonly used methylammonium lead triiodide, the bandgap changes significantly from 1.55 eV to 2.3 eV, and the material becomes more stable in air. Other changes to the composition include the replacement of the small organic molecules or elements by longer organic molecules, which can lead to the formation of two-dimensional metal halide perovskites. The large number of combinations of elements and molecules leads to an extensive list of possible compounds, each with their own properties. The work described in this thesis focuses on the characterization of various metal halide perovskites and their application in devices.

In *Chapter 2* methylammonium lead triiodide (MAPbI_3) was used as the active layer in solar cells. These MAPbI_3 solar cells typically suffer from hysteresis when they are used in the n-i-p structure, where the perovskite layer (i) is deposited on top of the electron transport layer (n). However, when a p-i-n structure is used, with MAPbI_3 on top of the hole transport layer (p), the hysteresis is reduced. The typical material used as hole transport layer, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate or PEDOT:PSS, leads to a low open-circuit voltage for the devices. Additionally, this layer is very sensitive to degradation. An alternative is nickel oxide (NiO_x), an inorganic material with higher stability, which leads to a higher open-circuit voltage. This Chapter describes how replacing the commonly used electron transport layer phenyl- C_{61} -butyric acid methyl ester, or PCBM, by a fulleropyrrolidine with a triethylene glycol monoethyl ether side chain (PTEG-1) can lead to higher power conversion efficiencies of perovskite solar cells with NiO_x as the hole transport layer. The reason for this increase is a higher short-circuit current density, which is caused by better charge extraction for PTEG-1, as confirmed by external quantum efficiency and photoluminescence experiments. Thickness optimization of the NiO_x and PTEG-1 layers led to a maximum power conversion efficiency of 16.1% for this type of solar cell.

Perovskite solar cell research progressed and researchers found better perovskites than MAPbI_3 to use as the active layer material. These alternatives would often lead to higher power conversion efficiencies and be more stable than MAPbI_3 . Their advantageous prop-

erties are derived from their composition, which typically use multiple halide ions and several organic or inorganic cations. However, if the perovskite is not structurally stable, the use of multiple ions can also lead to segregation of the elements, which is an unwanted effect. Studies on the structural stability of metal halide perovskites were underrepresented, and the few reports that were there mainly focused on thin films. The downside of this method is that thin films contain relatively many defects, which also affect the stability of the material. A study on the structural stability and photophysical properties of mixed cesium-formamidinium (FA) lead halide perovskites of the $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{3-x}\text{Br}_x$ family is reported in *Chapter 3*. In this study, we looked at a composition ($\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$) that is stable in single crystal form, which enabled us to circumvent the potential problems with morphology, since single crystals typically have fewer defects. We synthesized the same material in thin film form and studied its photophysical properties and structural stability and compared it to another, similar composition ($\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$) in thin film form, which was not reported before. We found that $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ has a lower crystalline quality in thin film form than $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$. Grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments revealed that the former has nanometer-sized domains of δ - CsPbI_3 and δ - FAPbI_3 , whereas $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ only has traces of δ - FAPbI_3 . The material with higher bromine content exhibited a reduced charge carrier lifetime in time-resolved photoluminescence experiments, which led us to conclude that this is the effect of δ - CsPbI_3 impurities. Considering that $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ has more favorable properties for the use in photovoltaic application, we synthesized this material in single crystal form to study its structural stability. Using X-ray diffraction, we could not find evidence for the impurities mentioned above and we concluded that the material is structurally stable and potentially interesting for the use in solar cells.

In the last two Chapters of this thesis, the focus is shifted from the three-dimensional lead-based perovskites to two-dimensional Ruddlesden-Popper perovskites with copper as the metal cation. These compounds have been studied for decades because they are known for their interesting behavior: they can exhibit effects such as thermochromism and piezochromism. Another property that can occur in these copper-based perovskites is photochromism, i.e. a reversible color change caused by the absorption of light. However, this phenomenon has seldomly been studied for this group of materials. In *Chapter 4*, we report the photochromic properties of bis(phenethylammonium) tetrachlorocuprate, or $(\text{PEA})_2\text{CuCl}_4$, for the first time. This material, which is yellow in the pristine state, turns brown when it is exposed to ultraviolet illumination ($\lambda = 254 \text{ nm}$) in a nitrogen environment. Using techniques such as Raman and X-ray photoelectron spectroscopy, GIWAXS and optical studies, we found that the color change is caused by two independent phenomena. The first is a Cu^{2+} reduction reaction and the second a transition from an octahedral copper-

chloride structure to square-planar CuCl_4^{2-} . The results from the GIWAXS experiments show that the structural order in the xy -plane of the film's surface is lost in the process. Upon air exposure, this structural order is restored, and the color of the film changes back to yellow. Interestingly, bis(methylammonium) tetrachlorocuprate, a similar compound, does not show photochromic behavior, which led us to conclude that the organic cation plays an important role in this phenomenon.

The diversity in applications of metal halide perovskites is shown once again in *Chapter 5*, where $(\text{PEA})_2\text{CuCl}_4$ is used to detect alcohol vapors. Previously demonstrated perovskite-based gas or vapor sensors were typically made with three-dimensional lead halide perovskites, but these tend to suffer from instability in various environments. Moreover, the use of lead can be harmful to nature and human life. We demonstrate that $(\text{PEA})_2\text{CuCl}_4$, after a treatment with ultraviolet illumination, can detect 1-propanol vapors in nitrogen. Detection of this compound is important because the presence of this alcohol in human breath is a potential marker for lung cancer. Our device, which is based on a change in conductance upon exposure to alcohol vapor, was capable to detect concentrations upwards of 2000 parts per million. Interestingly, fluctuations in the concentration on the order of 100 ppm could be detected at high concentrations (around 8000 ppm). This suggests that future research could lead to devices capable of detecting lower concentrations. The devices are stable in nitrogen, but their conductance decreases when they are exposed to air. This effect can be reversed by exposure to ultraviolet illumination, which makes the devices reusable.

Samenvatting

Hybride organisch-anorganische metaalhalideperovskieten vormen een veelzijdige groep binnen de organisch-anorganische hybride materialen. Dit komt tot uiting in de diversiteit aan apparaten die gebruik maken van deze perovskieten, zoals zonnecellen, leds, lasers en gassensoren. Dit brede scala aan toepassingen is mogelijk doordat de optische, elektrische en overige materiaaleigenschappen van een perovskiet aangepast kunnen worden door de chemische samenstelling te veranderen. Een voorbeeld is het vervangen van jodide-ionen door bromide-ionen in de veelgebruikte perovskiet methylammoniumloodtri-jodide, waarbij de bandkloof significant verandert van 1.55 eV naar 2.3 eV. Daarnaast is de bromide-variant stabiel in lucht. Een ander voorbeeld van een verandering aan de compositie is het vervangen van de kleine organische moleculen of elementen door langere organische moleculen, waardoor tweedimensionale metaalhalideperovskieten gevormd kunnen worden. Het grote aantal combinaties van elementen en moleculen zorgt voor een lange lijst van mogelijke materialen, die elk hun unieke eigenschappen hebben. Het onderzoek dat beschreven is in dit proefschrift legt de nadruk op de karakterisatie van verscheidene metaalhalideperovskieten en hun toepassing in apparaten.

In *Hoofdstuk 2* is methylammoniumloodtri-jodide (MAPbI_3) gebruikt als de actieve laag in zonnecellen. Deze zonnecellen hebben vaak last van hysteresis als ze gebruikt worden in een n-i-p-structuur, waarbij de perovskietlaag (i) op de elektrontransportlaag (n) wordt gemaakt. Wanneer echter sprake is van een p-i-n-structuur, met MAPbI_3 boven op de gattransportlaag (p), treedt er minder hysteresis op. Het gebruik van poly(3,4-ethyleendioxythiofeen):polystyreensulfonaat (ook wel PEDOT:PSS genoemd), een standaardmateriaal voor de gattransportlaag, leidt tot een lage nullastspanning voor deze p-i-n-apparaten. Een tweede nadeel van dit materiaal is dat het erg gevoelig is voor degradatie. Een alternatief is nikkeloxide (NiO_x), een anorganisch materiaal met hogere stabiliteit, dat voor een hogere nullastspanning kan zorgen. Dit Hoofdstuk beschrijft hoe het rendement van perovskietzonnecellen met nikkeloxide als gattransportlaag verhoogd kan worden door de veelgebruikte elektrontransportlaag fenyl- C_{60} -boterzuurmethylester, of PCBM, te vervangen door een fulleropyrrolidine met een triethyleenglycolmonoethylether-zijketen (PTEG-1). De oorzaak van deze toename is een hogere kortsluitstroombichtheid. Metingen aan het extern kwantumrendement en fotoluminescentie-experimenten laten zien dat dit veroorzaakt wordt door betere extractie van de ladingsdragers wanneer PTEG-1 gebruikt wordt als transportlaag. Na optimalisatie van de diktes van NiO_x en PTEG-1 kwam onze

zonnecel uit op een rendement van 16.1%.

Het onderzoek naar perovskietzonnecellen vorderde, en wetenschappers vonden perovskieten die beter werken als actieve laag dan MAPbI_3 . Deze alternatieve perovskieten kunnen vaak hogere rendementen behalen, daarnaast zijn deze materialen regelmatig stabielere dan MAPbI_3 . Hun superieure eigenschappen zijn het gevolg van hun samenstelling, waarin vaak meerdere halide-ionen en organische of anorganische kationen worden verwerkt. Desondanks kan het gebruik van meerdere ionen ook leiden tot segregatie van de elementen, een ongewenst proces dat plaats kan vinden als de structuur van de perovskiet niet stabiel is. Deze structuurstabiliteit was een onderbelicht aspect van het onderzoek naar metaalhalideperovskieten, waarbij men zich in het geringe aantal artikelen dat hierover geschreven is zich vooral richtte op dunne lagen. Het nadeel van deze methode is dat dunne lagen naar verhouding veel defecten bevatten, die de stabiliteit van het materiaal beïnvloeden. Een onderzoek naar de structuurstabiliteit en fotofysische eigenschappen van loodhalideperovskieten met een combinatie van cesium en formamidium (FA) als kationen (onderdeel van de $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{3-x}\text{Br}_x$ familie) is beschreven in *Hoofdstuk 3*. Hierbij keken we naar een samenstelling ($\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$) die stabiel is als monokristal, waardoor eventuele problemen als gevolg van de morfologie werden omzeild omdat monokristallen doorgaans minder defecten bevatten. We maakten vervolgens hetzelfde materiaal in dunne lagen en bestudeerden de fotofysische eigenschappen en structuurstabiliteit, en vergeleken deze met die van een soortgelijke, nog niet gepubliceerde compositie ($\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$) in de vorm van een dunne laag. We ontdekten dat $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ van lagere kristallijne kwaliteit is als dunne laag dan $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$. Experimenten met verstrooiing van röntgenstraling (GIWAXS) toonden aan dat onze dunne laag van $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.4}\text{Br}_{0.6}$ op een nanometerschaal domeinen bevat van $\delta\text{-CsPbI}_3$ en $\delta\text{-FAPbI}_3$, terwijl $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ alleen sporen van $\delta\text{-FAPbI}_3$ bevat. De levensduur van ladingsdragers, die bepaald werd met behulp van tijdsafhankelijke fotoluminescentie-experimenten, bleek lager voor het materiaal met hoger bromidegehalte, waardoor we concludeerden dat dit het gevolg is van de aanwezigheid van $\delta\text{-CsPbI}_3$ -domeinen. Aangezien $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.55}\text{Br}_{0.45}$ gunstigere eigenschappen heeft voor toepassing in zonnecellen hebben we dit materiaal gegroeid als monokristal om de structuurstabiliteit te kunnen bestuderen. We konden met röntgenkristallografie geen aanwijzing vinden voor de aanwezigheid van de bovengenoemde verontreinigingen en concludeerden dat het materiaal stabiel is en potentieel interessant voor het gebruik in zonnecellen.

In de laatste twee Hoofdstukken van dit proefschrift verleggen we onze aandacht van de driedimensionale loodhalideperovskieten naar tweedimensionale Ruddlesden-Popper-perovskieten met koper als metaalion. Deze materialen worden al tientallen jaren bestudeerd vanwege de interessante effecten die erin kunnen optreden, zoals thermochromisme

en piëzochromisme. Een verwant fenomeen is fotochromisme, een reversibele kleurverandering veroorzaakt door het absorberen van licht. Dit fenomeen is echter amper bestudeerd voor deze groep materialen. In *Hoofdstuk 4* wordt het fotochrome gedrag van bis(fenethylammonium) tetrachlorocupraat, ook wel $(\text{PEA})_2\text{CuCl}_4$ genoemd, voor de eerste keer beschreven. Dit materiaal is oorspronkelijk geel maar kleurt bruin na blootstelling aan ultraviolette straling ($\lambda = 254 \text{ nm}$) in stikstof. Technieken als Ramanspectroscopie, röntgenfoto-elektronspectroscopie, GIWAXS en andere optische experimenten tonen aan dat de kleurverandering veroorzaakt wordt door twee onafhankelijke fenomenen. Het eerste fenomeen is een reductie van Cu^{2+} , en het tweede een overgang van een octaëdrische koperchloridestructuur naar vierkant planair CuCl_4^{2-} . De GIWAXS-metingen laten zien dat de kristalstructuur in het xy -vlak aan het oppervlak van de laag verloren gaat in het proces. Na blootstelling aan lucht wordt deze kristalstructuur hersteld, waarbij de kleur van de laag terugverandert naar geel. Opmerkelijk is dat bis(methylammonium) tetrachlorocupraat, een vergelijkbaar materiaal, geen fotochrome eigenschappen heeft. Hierdoor concluderen we dat het organische kation een belangrijke rol speelt in dit fenomeen.

De diversiteit in toepassingen van metaalhalideperovskieten wordt nog eens onderstreept in *Hoofdstuk 5*, waarin $(\text{PEA})_2\text{CuCl}_4$ is gebruikt om alcohol dampen te detecteren. Het maken van gas- of dampsensoren met metaalhalideperovskiet is niet nieuw, maar deze sensoren waren voorheen voornamelijk gebaseerd op driedimensionale loodhalideperovskieten, die vaak instabiel zijn in verschillende omgevingen. Daarnaast kan het gebruik van lood schadelijk zijn voor de natuur en de mens. We tonen aan dat $(\text{PEA})_2\text{CuCl}_4$, na een behandeling met ultraviolet licht, 1-propanoldampen kan detecteren in stikstof. Het kunnen detecteren van deze alcohol is belangrijk omdat de aanwezigheid van deze stof in uitgeademde lucht een mogelijke indicatie is van longkanker. Ons apparaat, dat gebaseerd is op een verandering in geleidbaarheid wanneer de perovskiet in contact komt met alcohol damp, kon 1-propanoldampen detecteren bij concentraties vanaf 2000 delen per miljoen, ook wel parts per million (ppm) genoemd. Aangezien we fluctuaties in de concentratie ter grootte van 100 ppm konden meten rond een hoge concentratie van 8000 ppm verwachten we dat verder onderzoek kan leiden tot gevoeliger apparaten. De apparaten zijn stabiel in stikstof, maar hun geleidbaarheid neemt af wanneer ze worden blootgesteld aan lucht. Dit effect kan worden teruggedraaid door ze te behandelen met ultraviolet licht, wat de apparaten herbruikbaar maakt.

Curriculum vitae

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