Using *in situ* optical spectroscopy to elucidate film formation of metal halide perovskites

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Abstract

The research interest in halide perovskites has gained momentum enormously over the last recent years, also due to the demonstration of high-efficient perovskite based optoelectronic devices. Prerequisite for such highly efficient devices is to realize high-quality perovskite layers, which requires deep understanding about the perovskite formation and good process control. In that context, *in situ* optical spectroscopy during the processing of halide perovskites has become increasingly popular. Even though being a relatively easily accessible yet powerful tool for studying perovskite formation, there exist some technical and analytical aspects that need to be considered to unfold its full potential. In this perspective, we give an overview of the latest developments in the field of *in situ* optical spectroscopy to control and better understand the film processing of halide perovskites. We highlight possibilities and pitfalls regarding the analysis of measured optical data, discuss the development of technical concepts and address future prospects of optical *in situ* spectroscopy.

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1. Introduction

Since the first report as efficient absorber material in solar cells,¹⁻³ the interest in halide perovskites has gained enormous momentum. To a large extent, this is because they combine the most desirable properties of inorganic and organic semiconductors. Like organic semiconductors, they can be deposited at room temperature, and even from solution, thus allowing for cost-efficient industrial production on the basis of existing technologies. However, in contrast to organic semiconductors, they order into crystalline morphologies with concomitantly delocalized states and a band structure like classical inorganic semiconductors. This implies that exciton binding energies are low⁴⁻⁵ and diffusion lengths of charges are high.⁶⁻⁷ Consequently, halide perovskites are highly valued for next generation optoelectronic devices such as solar cells,⁸ light emitting devices (LEDs),⁹ and ionization radiation detectors.¹⁰⁻¹² Since halide perovskites assemble into crystalline structure during the formation of a film, the resulting final morphology of the perovskite layer is decisive for their optoelectronic properties, and thus the efficiency of perovskite-based devices.¹³ Accordingly, it was mainly morphology optimizations, enabling perovskite solar cells to achieve ever-higher record efficiencies so rapidly.¹⁴

Typically, the morphology of a perovskite layer depends decisively on the processing method and in particular on the exact timing of each step in the process. The high sensitivity of perovskite's functionality to the timings during processing, can also be regarded as a reason for the still limited reproducibility of perovskite solar cell efficiencies.¹⁵ In the past, labor-intensive approaches to optimize the perovskite layer have been pursued, where optimization steps were mostly inferred retrospectively from the characterization of the final thin film.¹⁶ In contrast, during the last few years, investigating and understanding the perovskite formation process during film processing started to attract attention.

Several studies addressed the film formation process with the help of *in situ* measurements. They mainly using scattering methods,¹⁷⁻²⁵ which allowed to identify the important role of e.g. additives, the exact process conditions, or the morphology of precursor layers.^{19, 26-31} In addition to scattering methods, other techniques such as optical spectroscopy are also suitable to study the formation of semiconductor films from solution.³²⁻³³ This is because the crystallographic structure of the perovskite is very sensitively linked to its electronic structure and thus to its optical properties. Hence, *in situ* optical spectroscopy has become increasingly popular, often complementing *in situ* scattering experiments, e.g. to identify different crystallization phases and their timing in the film formation process.^{29, 34-35} In addition, driven by *in situ* optical characterizations, some studies could gain more detailed insights about the nucleation and growth dynamics, or about the perovskite growth at the early stage of film formation.³⁶⁻³⁷ Recently, we and others investigated the formation of perovskites in

detail by simultaneous measurement of photoluminescence (PL) and absorption or reflection, further demonstrating the potential of optical *in situ* spectroscopy during processing of halide perovskites.^{38-³⁹ Spurred by recent technological and analytical advances,^{38, 40} optical *in situ* monitoring during film processing has become relatively easily accessible. It thus has significant potential as a versatile and cost-effective investigation method, especially in comparison with time-resolved scattering investigations, which typically can only be carried out at suitable beamlines.}

In this article, we give an overview of recent developments in the field of optical *in situ* spectroscopy for investigating perovskite film formation, and we also highlight possible future perspectives. First, we focus on the basic optical properties of halide perovskites and which information can be extracted from them (Section 2). In Section 3, we give an overview over technical developments to measure the optical properties during processing, such as spin coating or slot die coating. Finally, we summarize recent developments and studies that use optical *in situ* spectroscopy either to improve processing control, or to better understand the film formation (Section 4).

2. Optical properties of halide perovskites and their measurement related artefacts

A simple method to probe the electronic structure of a semiconductor is to measure its absorption spectrum. To do so, typically white light with intensity I_0 is irradiated onto the sample, where the light is either transmitted (*T*), absorbed (*A*), scattered (*S*) or reflected (*R*):

$$I_0 = T + A + S + R \tag{1}$$

In the absence of scattering, the absorption can be calculated from transmission and reflection data. If the fraction of reflected light is small, e.g. upon perpendicular incidence of the white light, it is possible to calculate the absorption of the sample by considering only transmission. For lead halide perovskites, the divalent metal and the halide mainly determine the electronic structure of the perovskite band edges,⁴¹⁻⁴⁴ leading to optical properties similar to traditional inorganic semiconductors like GaAs.⁴⁵⁻⁴⁶ The absorption spectrum of lead halide perovskites can be decomposed into different contributions, as indicated in Figure 1a.⁴⁶⁻⁴⁷

One contribution is the band-to-band absorption (red dotted line in Figure 1a), which starts at the material-characteristic band gap energy. In addition, excitonic absorption features are present and superimpose the band-band absorption. Excitons are electron-hole-pairs bound by Coulomb interaction.⁴⁸ This interaction results in bound states below the band gap (blue line in Figure 1a) and also in continuum states above the band gap (red dashed line in Figure 1a).⁴⁹ The absorption spectrum

of halide perovskites can be described by Elliott's theory, from which it is possible to extract parameters such as the exciton binding energy and the band gap energy.⁴⁹ The band gap is often also determined using a Tauc plot. There, it is assumed that the absorption is $\sim \sqrt{E}$ for a direct optical transition, so that plotting the square of the absorption versus energy results in a straight line. In such a Tauc plot, the crossing point of a linear fit to the absorption onset with the energy axis determines the band gap. For an indirect transition, the square root of the absorption needs to be taken instead of its square, due to the different spectral dependence of direct and indirect transitions. However, since the excitonic absorption masks the band-to-band transition (Figure 1a), the use of a Tauc plot is inappropriate to determine the absolute band gap energy for typical halide perovskites. It though may be used to quantify changes in absorption onsets.^{46, 50}

Apart from band-to-band and excitonic absorption, there exists a tail state absorption, which extends far below the band gap of the semiconductor.⁵¹⁻⁵³ Here, a typical example is the so-called Urbach tail, with an exponentially decreasing absorption coefficient towards lower energies (Figure 1b).⁵⁴⁻⁵⁵ While the exact mechanism causing this exponential decrease is under debate, there is general consensus that electron-phonon interaction as well as static disorder influence the slope of the Urbach tail.^{52-53, 56-60} Even though the Urbach tail contains valuable information, it is challenging to access it directly in an ordinary absorption measurement, due to limited setup sensitivities.



Figure 1: (a) Decomposition of a semiconductor absorption spectrum according to Elliott's theory into band-to-band absorption in the free electron picture (red dotted), absorption of bound states of the exciton (blue) and absorption of the excitonic continuum (red dashed). Reprinted with permission from ref. 46. Copyright 2018, the authors. (b) Absorption coefficient \propto of MAPbI₃ as determined by (red symbols) photothermal deflection (PDS) and (red solid) calculated from the PL (black symbols) according to Equation 2. Adapted with permission from ref. 55. Copyright 2016, the American Physical Society.

However, the Urbach tail is also reflected in the shape of the PL spectrum, since the latter relates to the absorption of the material. The radiative recombination of free holes and electrons can be described (in case of spatially homogeneous charge carrier distribution) as⁶¹⁻⁶²

$$PL(E) \propto a(E) \cdot E^2 \cdot \exp\left[-\frac{E}{k_B T}\right] \cdot \exp\left[\frac{\mu}{k_B T}\right]$$
 (2)

Where α is the absorbance, k_B is the Boltzmann constant and T is the temperature. μ represents the quasi-fermi level splitting (sometimes also labelled $\Delta\mu$), which is the splitting between the quasi-fermi levels of the electrons in the conduction and in the valence band. Equation 2 implies that the absorption coefficient of a perovskite can be calculated from PL measurements. A comparison of the absorption calculated from PL with absorption measured by photothermal deflection spectroscopy is shown in Figure 1b.⁵⁵ Furthermore, with the absolute PL intensity or the PL quantum yield (PLQY), it is possible to extract μ by⁶³⁻⁶⁴

$$\mu = \mu_{rad} + k_B T \cdot \ln(PLQY), \tag{3}$$

where μ_{rad} is the quasi-fermi level splitting in the radiative limit. μ reflects the highest achievable open circuit voltage (V_{oc}) of a device that includes the investigated material as active layer. Therefore, it is also referred to as implied V_{oc} .

At this point, some brief consideration of the PLQY (or PL intensity) is useful. Charge carrier recombination can be described by a rate equation accounting for monomolecular (defect assisted, $\sim n$), bimolecular ($\sim n^2$) and Auger ($\sim n^3$) recombination, with only the bimolecular recombination occurs radiative.⁶⁵ Due to the different dependencies of the individual recombination mechanisms on the charge carrier density n, also the PLQY is a function of n.⁶⁵ Thus, without the knowledge about the charge carrier density present in the experiment, a measured PLQY value has only a limited validity to assess the quality of a sample. For example, even under identical experimental conditions (especially laser fluence), a higher n can be present in a polycrystalline sample due to more limited charge carrier diffusion as compared to a highly crystalline thin film with large grain sizes.

The models mentioned above describe the intrinsic optical properties of the material. In reality however, optical effects alter measured spectra. One possible effect is a sinusoidal modulation of the absorption (or transmission) spectra due to white light interference, as illustrated in Figure 2a. Depending on the thickness of the layer and the wavelength of the light (indicated by the color of the arrows in Figure 2a), the directly transmitted light (thick arrow on top) can interfere either positively (indicated by "+" for the orange arrows) or negatively (indicated by "-" for the green arrows) with the internally reflected light (thin arrows on top). Positive interference leads to a decrease in the OD, while negative interference leads to an increase. Interference can be caused e.g. by a wet solvent layer which

becomes thinner upon drying. If the refractive index of the layer causing the interference is known, the layer thickness d can be calculated from the spectral position of two adjacent extrema according to^{24, 66}

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)},\tag{4}$$

where $\lambda_{1,2}$ are the wavelengths at which two neighboring extrema occur and $n_{1,2}$ are the refractive indices at $\lambda_{1,2}$.

Another aspect affecting the absorption spectra is the surface coverage of the sample, i.e. how much of the investigated sample area is covered by perovskite (see Figure 2b and c).⁶⁷ An incomplete surface coverage is likely to be present at the beginning of a film formation process. This incomplete coverage results in a lower overall absorption intensity, and, notably, it can cause an apparently distorted absorption spectrum where the high energy region appears flatter (see Figure 2c). This artefact is a direct result from white light passing the uncovered areas of the sample. It can be deduced by correct application of the Lambert Beer law by considering that a fraction of the white light is partly absorbed by the perovskite and the rest of the light is transmitted at uncovered areas without being absorbed.⁶⁷ Additionally, an incomplete surface coverage leads to increased light scattering at perovskite crystallites, resulting in an overall lift of the baseline in measured absorption spectra. Measuring the latter in an integrating sphere minimizes the influence of scattering (Figure 2b).

A further optical effect relates to the crystal thickness. When the crystal thickness of the investigated perovskite sample increases, then the measured absorption spectra become more step like. This is because the fraction of white light passing the sample at the uncovered areas (or the dark current of the detector) determines an upper limit of the detectable absorption. If the absorption of the material exceeds this value, the recorded absorption spectrum is "cut off" at this upper limit. Due to the finite decrease of the absorption coefficient below the band gap, this cut-off happens at lower energies for increasing samples thickness. When such absorption spectra are normalized, the band edge appears shifted to lower energies, due to this optical effect. Thus, a red shift of the absorption edge with increasing perovskite thickness is an optical artefact and not necessarily due to a change of the fundamental band gap. This should be taken into account before associating an absorption shift with a change in band gap energy.

Although it is not meaningful to extract a film thickness from such absorption spectra, it can still be possible to quantify the coverage ratio and average crystal height, as detailed by Tian et al..⁶⁷

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Figure 2: (a) Absorption spectrum with optical density modulations due to interference effects. The inset sketches the interference effect at a thin layer. The arrows in different colors indicate light with different wavelength, leading either to positive ("+") or negative ("-") interference caused by reflections at interfaces. (b) Absorption spectra of a perovskite film with incomplete surface coverage for different measurement setups. The blue line shows the absorption of an individual crystal measured with an optical microscope. Inset: microscopy image of the investigated perovskite film. (c) Calculated absorption spectra for decreasing surface coverage ratio *6* based on the absorption spectrum of an individual perovskite crystal from (b). (b,c) Reprinted with permission from ref. 67. Copyright 2015, American Chemical Society. (d) left: sketch illustrating prolonged PL paths in a crystal due to internal reflections. Right: resulting PL spectrum, consisting of a contribution due to direct PL (Peak 1) and filtered PL (Peak 2) resulting from self-absorption. Reprinted with permission from ref. 68. Copyright 2020, the Royal Society of Chemistry. (e) PL peak position (symbols) as a function of film height for MAPbl₃ thin films with different thicknesses. The dashed line is a fit according to Equation 5. Reprinted with permission from ref. 69. Published by the Royal Society of Chemistry.

Not only absorption, but also measured PL can deviate from the intrinsic PL properties. For example, PL spectra of halide perovskites can – depending on the measurement conditions and layer thickness – heavily be influenced by self-absorption. This strong re-absorption of emitted light results from the refractive index difference between the perovskite layer and air or glass interface. The refractive index of halide perovskites (~2.5 for methyl ammonium lead iodide (MAPbl₃))⁷⁰ typically is significantly higher than the refractive indices of the surrounding media (e.g. for a fused silica substrate ~1.45 at the wavelength of the PL of MAPbl₃)⁷¹, which leads to a high probability for internal PL reflections, as can be deduced from the Fresnel equations. This in turn can cause multiple internal reflections of the emitted light and concomitantly a long optical path length. Due to this long optical path, the low absorption at the absorption onset becomes nevertheless relevant, as it reabsorbs the high-energy part of the emitted light, thus apparently shifting the PL peak to lower energies. This effect is accompanied by a reduced PL intensity (i.e. PL quantum efficiency) and can lead to additional PL features such as shoulders or distinct peaks at lower energies (see Figure 2d).^{68, 72-76} Even in perovskites thin films, the effect of self-absorption on measured PL can be surprisingly strong as the optical path lengths within the perovskite can be significantly longer than the film thickness. Obviously, the surface

roughness of the perovskite also influences the reflection probability, changing the light in- and outcoupling.^{73, 77} Depending on which parameters should be extracted from the PL, self-absorption needs to be considered quantitatively by optical modelling.^{69, 72, 78-80} We note that the extend of self-absorption on measured PL typically is sensitive to the specific measurement geometry. This allows to identify self-absorption effects in the PL spectrum by changing the measurement geometry.^{75, 78}

In addition to optical effects that alter measured PL spectra, changes of the semiconductor's electronic structure also influence its intrinsic PL properties. A relevant effect in the context of film formation is quantum confinement. It is present if perovskite crystallites are very small, i.e. ≤ 25 nm. Then the PL shifts to higher energies compared to the bulk material (Figure 2e).⁶⁹ The shift can be understood in terms of a quantum mechanical particle in a box model. There, the energy levels (and thus their difference) depend on the square of the size of the box. As illustrated in Figure 2e, the PL peak position *E* can be related to the crystallite size *d* according to⁸¹

$$E = E_g + \frac{b}{d^2},\tag{5}$$

where E_g is the bulk PL peak position and *b* is a constant, which was reported to be in the range of $1 - 5 \text{ eV/nm}^2$ for MAPbI₃.^{69, 82} Thus, if *b* and E_g are known, the size of the crystallites can be estimated from the PL peak position. It is also possible that the PL intensity increases with increasing confinement, which was frequently explained by an increased overlap between electron and hole wavefunction.⁸³⁻⁸⁶ If confinement and a size-dependence of the PL intensity are present, a distribution of crystal sizes leads to an asymmetric broadening of the measured PL peak.^{85, 87} Confinement effects during thin film processing are most likely to occur at the beginning of the perovskite formation.

Additionally, strain e.g. introduced by a substrate can alter the electronic structure of the perovskite.⁸⁸⁻⁹¹ In contrast to quantum confinement, the presence of strain can lead to band gap (or PL peak) shifts to higher but also to lower photon energies,⁸⁸⁻⁹¹ as two different effects can occur: a decrease in the Pb-X bond length, which was found to decrease the band gap energy, and a strain-induced decrease of the Pb-X-Pb bond angle causing an increase of the band gap.⁸⁸⁻⁹⁰ Even though both, changes in strain and quantum confinement can easily occur simultaneously during perovskite processing, it is possible to distinguish the individual effects as they impact the PL in different ways. While quantum confinement occurs only for crystal sizes below ~25 nm, strain is not limited to small crystallites. Furthermore, quantum confinement is often leading to an increased PL intensity and asymmetrically broadened PL peak shape.^{85, 87} This is in contrast to strain, which - to the best of our knowledge – does not lead to higher PL intensities, but rather strain induced PL decrease was found recently.⁸⁸

Another cause for a spectral shift of the PL peak (and the absorption onset) can be a change of stoichiometry in the perovskite's composition. For example, the band gap of lead halide perovskites can be tuned continuously from 1.55 eV to 3.15 eV by changing the halides, i.e. by mixing iodine with bromine and bromine with chlorine.⁹²⁻⁹⁵ Since it is well possible that different halides incorporate into the perovskite crystal with different speed, a change in halide ratio can occur during film formation as well.⁹⁶

When interpreting the optical changes that are observed *in-situ* in the course of perovskite formation from a solution, it is important to be aware of the above-mentioned optical effects that can impact on absorption and PL spectra.

3. Technical approaches to record optical signals in situ during film formation

Before focusing on specific approaches to monitor optical properties during the processing of halide perovskites, it is worthwhile to consider briefly what might technically limit the proper detection of optical spectra. One important aspect is that halide perovskites often exhibit a low PLQY at relevant processing temperatures (e.g. room temperature or higher).⁹⁷ Thus, for excitation intensities that are sufficiently low to avoid perovskite degradation or structural changes, the PL spectra can suffer from a relatively poor signal to noise (S/N) ratio. Similarly, in case of transmission or absorption measurements, a poor S/N ratio can result from strong absorption of the perovskite or weak light intensity of the white light source. In steady-state measurements, one can overcome these limitations by using a sufficiently long exposure time for light detection, or by averaging a large number of individual measurements. This, however, is not possible for in situ optical spectroscopy, where spectra are taken several times per second and thus the exposure or integration time for a spectrum is limited by the rate with which the subsequent spectra are taken. In many cases, depending on the perovskite film formation route, at least a sub-second time resolution is required. Therefore, most studies in the past used state-of-the-art charge-coupled devices (CCDs) with a sub-second repetition rate for light detection. An obvious way to overcome the limitation on the light accumulation time available for each spectrum during in situ measurements is to increase the intensity of the light source. This works as long as the impinging light intensity does not damage the sample or significantly affect the film formation dynamics, e.g. due to laser heating. This condition is easier to meet for the white light sources employed in transmission measurements than for the laser irradiation required for PL studies. This is one of the reasons why in the past, in situ measurements to study the film formation of halide perovskites were preferably conducted merely for absorption.^{29, 36, 98-100}

Generally speaking, the smaller the power density of the incident light (be it white light or laser light), the less light-induced sample degradation occurs. When leaving the power of the incident light constant, it thus can be beneficial to increase the size of the irradiation spot, which decreases the power density while the overall signal can stay roughly constant. In this context, also the use of optics with high collection efficiency, in combination with large size photodetectors is beneficial to minimize the necessary excitation power density while maintaining an appropriate S/N ratio.

For *in situ* transmission measurements, the technical challenge is to place either the white light source or the components for light detection below the sample in the setup used for processing, e.g. in a spin coater or slot die coater. In many cases, this makes it necessary to modify existing setups extensively or even to pursue a self-construction. In 2014, Abdelsamie et al. presented a homebuilt spin coater with a hole in the center of the rotating chuck, and with enough space underneath to install an optical fiber. With the help of this fiber, the white light transmitted from above the sample was directed into a spectrograph.¹⁰¹ Using this setup enabled the investigation of the film formation of various solutionprocessed semiconductors such as organic semiconductors and hybrid perovskites.^{98, 101-102}



Figure 3: (a) Schematic representation of a spin-coater device, capable for measuring transmission and PL during spinning. Reprinted with permission from ref. 40. Copyright 2018, American Chemical Society. (b) Illustration of a wide-field microscope setup, to measure transmission spectra superimposed with PL. Considering reference measurements, individual spectral contributions (Absorption and PL) can be extracted. Reprinted with permission from ref. 103. Copyright 2019, American Chemical Society. (c) Schematic of the optical monitoring process to simultaneously measure transflectance (by halogen Lamp) and PL (excited by 455 nm LED) spectra. Reprinted with permission from ref. 38. Published by The Royal Society of Chemistry. (d) Schematic illustration of the main components of a detection system for the quasi-simultaneous measurement of absorption and PL using one spectrometer, with the operation states during

absorption (top) and PL (bottom) measurement. Components are: Chopper wheel (1), optical fiber (2,5), lenses (3,4), optical filter (6), mirrors (7,8). Reprinted with permission from ref. 40. Copyright 2018, American Chemical Society.

In 2018, we built a spin coater with a reversed geometry, where the white light is placed below the rotating chuck and the optical fiber for light detection is located above the sample (Figure 3a).⁴⁰ This geometry allows for the quasi-simultaneous detection of absorption and PL as detailed further below. To measure the PL precisely and to minimize self-absorption effects, the sample needs to be excited on the same side from which the PL is detected. One realization for this is that the incident excitation light and the fiber collecting the PL are both above the perovskite/air interface (Figure 3a). If the layer supporting the perovskite film does not cause PL quenching, then it is also possible to invert the measurement geometry as shown in Figure 3b. This is the case, e.g. if the perovskite is deposited directly on a glass substrate, without any material underneath such as a typical charge transport layer materials would cause PL quenching. Such a measurement setup was recently presented by Hong et al..¹⁰³ There, white light shines through the perovskite layer from above for the transmission measurement. The PL is excited from below the sample by a continuous wave (CW) laser beam in the fashion of a confocal PL microscope. The PL that emits into the lower half space and the transmitted white light are both collected by the microscope objective and directed into a spectrograph. As a result, one detects a transmission spectrum of the halogen lamp through the perovskite layer, superimposed by the perovskite PL. By measuring the transmission also without laser excitation, the spectral contributions of the PL and the transmission can be separated. Since the reference absorption to determine the PL can change over time due to structural dynamics of the perovskites, it is necessary to record transmission spectra without PL excitation repeatedly. Thus, the measurement of the PL has to be interrupted repeatedly for a certain time span. Hence Hong et al. used this method to study changes of optical properties on longer time scales, i.e. minutes to hours and investigated perovskite degradation due to environmental influences.¹⁰³ In his work, the simultaneous monitoring of PL and absorption allowed to differentiate structural degradation of the perovskite from changes in the electron-hole recombination mechanism. This nicely demonstrates the potential to gain deeper insights when considering both, PL and absorption.¹⁰³

Apart from absorption and PL, also PL excitation spectroscopy was recently used to investigate the degradation of lead halide perovskites in a microscope setup.¹⁰⁴⁻¹⁰⁵ Here, the PL intensity is monitored as a function of excitation wavelength. By also measuring the transmitted excitation light, the absorption of the sample can be calculated, which then enables calculating wavelength dependent changes in the PLQY. With this approach Merdasa et al. could identify a transition range between MAPbI₃ and PbI₂, at which charge carriers accumulate.¹⁰⁴

The PL and absorbance can be measured simultaneously on shorter time scales and with higher detection rates when using different, dedicated detectors for PL and absorption. This can be implemented in several ways.

In 2016, Engmann et al. presented a setup where a diode laser excites the PL of the sample from above, while white light is directed onto the sample at an angle matching the substrate's Brewster angle.¹⁰⁶ Thus, both the light transmitted through the sample and the light reflected by the sample could be detected separately, using additional polarizers in front of the different spectrographs. This allowed studying the temporal evolution of PL, absorption (calculated based on transmitted white light) and film thickness (calculated based on reflected white light, see eq. 4) during blade coating of different organic semiconductor blends.¹⁰⁶ To avoid scattered white light disturbing PL spectra, it is necessary to probe PL and transmission or reflection not at the same sample spot, but slightly offset from each other. This is sufficient for processing methods such as blade coating or slot coating, where the drying proceeds along one specific direction.

Recently Suchan et al. investigated the perovskite formation of MAPbl_{3-x}Cl_x during annealing, using a homemade setup to measure PL and reflected white light from the same sample area (Figure 3c).³⁸ Interesting here is that the bottom side of the sample substrate is mirrored. If the white light enters the detector after reflection at this mirrored bottom side, it is transmitted through the perovskite as well. The authors call this transflectance, which also contains information of the perovskite absorption.³⁸ From a technical viewpoint this is elegant since all components of the measurement setup can be placed above the sample, so that less technical modifications of existing processing setups are needed to implement the measurement system. Recently, also Rehermann et al. used this measurement concept to determine transflectance during spin coating and subsequent annealing of mixed halide perovskites of the type MAPb(I_xBr_{1-x})₃.¹⁰⁷

To reduce the technical effort for the measurement of different optical signals, we developed an optical detection system that allows measuring PL- and absorption spectra quasi-simultaneously by means of one single detector unit consisting of spectrograph coupled to a CCD-camera.⁴⁰ Figure 3d shows a schematic of the measurement concept. A rotating chopper blade with mirrored segments represents the conceptual centerpiece. With that, it is easily possible to alternate between two different beam paths: During the detection of an absorption spectrum, the laser diode is switched off and the white light LED is switched on. The light transmitted through the sample is reflected at the mirrored chopper blade segments and directed straight into a spectrograph (Figure 3d top). In contrast, during PL detection, the laser diode is switched on, the white light LED is switched off, and the chopper blade is in such a position that the PL passes through an empty chopper segment (Figure 3d bottom). This way, PL enters an extended optical path that includes an optical filter to block

any unwanted remaining laser signal. The filtered PL finally is directed into the spectrograph *via* deflection mirrors. A microcontroller ensures the correct timing between the on and off states of laser diode, white-light, and chopper blade position. The maximum rate for detecting pairs of PL and absorption depends mainly on the maximum detection frequency of the CCD camera used. In our case, it was possible to detect pairs of PL and absorption with a rate of up to 15 Hz, i.e. with a minimum acquisition step time of ~67 ms, allowing to resolve all typical film formation dynamics of organic semiconductors and halide perovskites.³⁹⁻⁴⁰

This brief, exemplary yet not exhaustive overview may serve to illustrate different concepts that can be employed to monitor optical signals during the processing of halide perovskites. By now, experimental approaches exist that require only a low number of technical components and that are relatively easy to implement in existing processing setups. This is an encouraging development, which facilitates the use of *in situ* optical monitoring for improving process control, both in the laboratory as well as in the industrial context. Moreover, these technological developments will make it easier to combine in-situ monitoring of optical signals with other *in situ* measurement techniques, e.g. *in situ* grazing incidence wide angle X-ray scatter (GIWAXS). The combination of several individual measurements into one time-resolved multimodal measurement allows for a detailed characterization of the sample evolution during processing.^{37, 108-109} Following how several properties evolve and correlating them has a high potential to elucidate the film formation of halide perovskites in a level of detail that was previously not possible.

There is, however, a further, only partially resolved technical aspect that is worth mentioning. The detection of optical spectra taken over a period of time can quickly generate large amounts of data due to high frame rates and/or long investigated time spans. These large data become difficult to deal with, so that it becomes necessary to find ways for their efficient processing, display and analysis. It is evident that this aspect will gain further importance in the area of *in situ* monitoring during film processing.

4. Recent developments regarding the characterization of the film formation process

4.1. In situ optical monitoring to determine timings of the film formation process

In situ spectroscopy of single optical properties was used repeatedly to monitor the timing of different steps in the perovskite crystallization process and to support the results from corresponding X-ray scattering measurements, for different solution processing methods and during annealing. Already in

2013, Burschka et al. tracked the conversion of Pbl₂ to MAPbl₃ in a sequential deposition method by in situ absorption and PL at characteristic wavelengths and observed the perovskite conversion to be complete after about 20 s.³⁴ This fast crystallization was enabled by the use of a porous TiO₂ scaffold, leading to perovskite solar cells with, at that time, a record efficiency of 15 %. Similarly, Barrit et al. used in situ absorption to investigate the influence of the PbI₂ precursor phase on the perovskite crystallization speed.²⁹ In this work, Pbl₂ films were loaded with a methyl ammonium iodide (MAI) solution, followed by an isopropyl alcohol (IPA) washing step. Using in situ GIWAXS measurements during spin-coating Pbl₂ from dimethylformamide (DMF) solution, the authors identified one disordered (P_0) and two ordered (P_1 , P_2) precursor phases before the dry PbI₂ film formed. Ex situ GIWAXS revealed that loading the precursor film with MAI during the P₂ phase already leads to a complete perovskite conversion of the film prior to annealing. To investigate this perovskite formation process, the MAI loading step during P₂ and for a dry PbI₂ film were monitored using *in situ* absorption measurements (Figure 4a). In case of MAI loading during the P₂ phase, perovskite absorption appeared quickly and saturated after about 20 s, indicating complete conversion. In contrast, when MAI was loaded on the dry PbI₂ film, the perovskite absorption grew significantly slower, implying a slower conversion. This was explained by a decreased uptake of MAI solution of the dry PbI₂ film. Finally, MAI loading during the P₂ phase led to devices with improved efficiency and higher reproducibility.



Figure 4: (a) *In situ* absorption during MAI loading on the P₂ precursor phase (top) and on the dry Pbl₂ film (bottom). Reprinted with permission from ref. 29. Copyright 2019, WILEY-VCH. (b) Temporal evolution of absorption intensities at 590 nm from *in situ* absorption measurements during spin coating of MA₃Bi₂I₉ without and with use of an anti-solvent (CB), dripped after 40 s of spin coating. Reprinted with permission from ref. 99. Copyright 2019, WILEY-VCH. (c) *In situ* absorption of MAPbI_{3-x}Cl_x during annealing (left). Corresponding temporal slices at a wavelength where the perovskite and the intermediate phase absorb are shown on the right. Reprinted with permission from ref. 100. Copyright 2014, American Chemical Society. (d) Temporal evolution of the PL intensity during annealing at different temperatures of a perovskite film deposited on a PEDOT:PSS layer (top). Solar cell efficiencies as a function of annealing time for different temperatures (bottom). The arrows indicate the coincidence of annealing time for maximum device efficiency and time at which the drop in PL intensity saturates. Reprinted with permission from ref. 110. Copyright 2016, WILEY-VCH.

Another example where *in situ* absorption was used for determining timings during perovskite processing is the work by Lee et al..⁹⁸ The authors built solar cells, where the perovskite layer was deposited by one-step solution processing without and with different additives. Based on the device performances and by atomic force microscopy, scanning electron microscopy (SEM) and optical microscope images, CHP (N-cyclohexyl-2-pyrrolidone) was identified to be the best additive for improving crystallization and device efficiency. To investigate the perovskite crystallization dynamics, *in situ* UV-Vis absorption was recorded during spin coating without additive and with CHP. With additive, the perovskite formation slowed down significantly, as could be concluded from considering

the absorption at a perovskite-specific wavelength. Furthermore, there was less contribution of scattering in the spectra, indicating smoother films. Corresponding *in situ* GIWAXS measurements showed that CHP inhibits the formation of PbI₂ solvate phase, thereby assimilating the crystallization rates of PbI₂ and MAI.

In situ absorption was used also in case of the solvent engineering method, where an anti-solvent is applied during the spin coating to initiate perovskite crystallization. Tang et al. compared the crystallization of MAPbI₃ with that of a Bismuth-based perovskite.⁹⁹ Using *in situ* GIWAXS measurements, they found that for natural drying, the Bismuth-based perovskite formed directly without an intermediate phase, in contrast to MAPbI₃. To gain more control over the crystallization process, an anti-solvent was dripped onto the wet solution during spin coating. This step was monitored using *in situ* absorption and analyzed by following the time dependence at a wavelength related to perovskite absorption (Figure 4b). Without anti-solvent dripping, the perovskite formation is slow and reduced, whereas it is fast and more complete when the anti-solvent is dripped at an appropriate time.

Also, the annealing of perovskite films was monitored by in situ absorption, e.g. by Unger et al. for the case of the PbCl₂ based MAPbI_{3-x}Cl_x crystallization (Figure 4c).¹⁰⁰ Directly from the beginning of the annealing process at 100 °C, an absorption feature at wavelengths below 650 nm started to gain intensity (Figure 4c), which they associated with intermediate phase absorption. For longer times, also absorption at higher wavelengths, indicative for the perovskite absorption, increased. Considering the evolution of absorption intensity at 560 nm (trace I in Figure 4c) and at 740 nm (trace P in Figure 4c) allowed to quantify the delay of the perovskite crystallization to be about 10 minutes. From these measurements it also became clear that the precursors fully converted to perovskite after 40 min. Similarly, van Franeker et al. investigated the annealing of MAPbl₃ films using in situ PL and absorption.¹¹⁰ Based on *in situ* absorption, they found that when stock solution and substrates were at room temperature, MAPbl₃ only formed during annealing on a time scale of 1 min, whereas upon using a hot solution (70 °C) and heated substrate (92 °C), the perovskite formed completely already during spin-coating. Despite complete perovskite formation during spin coating, the non-annealed hot-casted films exhibited small grains resulting in low solar-cell performance. Annealing improved the solar cell performance significantly, which was explained by an increased charge carrier mobility, whereas annealing for too long was detrimental. The authors investigated the increase of the mobility during annealing by monitoring in situ the evolution of perovskite PL intensity of samples processed on a quenching layer (here PEDOT:PSS) (Figure 4d). Upon photo-excitation from the top, carriers are generated near the surface and then diffuse into the bulk. With increasing mobility, more carriers can reach the quenching layer at the bottom, leading to a drop of measured PL intensity. The authors found

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that the drop of PL intensity saturates after a certain annealing time, depending on the temperature (Figure 4d middle). Since excitation fluence and film thickness were kept constant, this saturation behavior indicates that further annealing does not lead to more carriers reaching the quenching layer. Interestingly this was also the annealing time, which lead to the best solar cell performances (Figure 4d bottom). This work thus underlines how powerful *in situ* optical spectroscopy can be for inline monitoring of perovskite processing.¹¹⁰

Another example where timings during the annealing step were monitored by *in situ* spectroscopy, here in addition to the spin coating step, is the work by Rehermann et al..¹⁰⁷ Driven by the question whether stoichiometric inhomogeneities are already introduced during film formation, they investigated the film formation of MAPb(I_xBr_{1-x})₃ for different halide ratios x using *in situ* transflectance and *ex situ* X-ray diffraction (XRD). From transflectance measurements, they inferred that pure MAPbBr₃, i.e. x = 0, crystallizes directly into the perovskite phase during spin-coating. However, for nominal halide ratios of x = 0.3 and 0.6, a bromine-rich perovskite phase crystallizes with x = 0.08 and x = 0.38 respectively, as inferred from the absorption onsets. For higher iodine contents, i.e. x = 0.7 and pure MAPbI₃, no perovskite phase but only a solvate phase is observed, identified by *ex situ* XRD. Based on the evolution of transflectance intensity associated to perovskite, they could find that the iodine delayed the perovskite formation for x = 0.3 and 0.6, while the bromine delayed the intermediate phase formation for x = 0.7 with respect to pure MAPbI₃. Upon annealing, also tracked by *in situ* transflectance and *ex situ* XRD, the perovskite continues to grow and finally reaches the correct halide ratio as initially introduced in the stock solution.

These examples demonstrate how improved control over the crystallization process can be obtained when monitoring the different steps in the crystal formation process. This also allows to choose the correct time for the addition of an additive, anti-solvent or the correct time for the start of a heating process.

4.2. Probing one individual optical property in situ to understand perovskite formation

In situ optical spectroscopy is not only suitable to determine the timing of certain film formation dynamics when accompanying *in situ* scattering investigations. Rather, optical *in situ* spectroscopic data was also the basis for further analysis and for better understanding the formation process. For example, Hu et al. monitored the drying behavior of a triple cation perovskite (Cs_{0.05}FA_{0.81}MA_{0.14}Pbl_{2.55}Br_{0.45}) (FA = formamidinium) in a DMF/DMSO (DMSO = dimethyl sulfoxide) mixture at room temperature using *in situ* absorption measurements.³⁶ In the course of a simple one-step processing, they could identify an intermediate phase occurring between the initial solution phase

and the final solid phase (Figure 5a). The intermediate exhibits a wavelength independent increase in absorption intensity, due to light scattering at structures with sizes in the range of the wavelength of the incident light. In contrast, for perovskite crystallization the measured absorption intensity increases more strongly in the shorter wavelength range, especially for below 700 nm (Figure 5a). Based on the timings of the film formation phases determined by the *in situ* monitoring, Hu et al. then used a nitrogen air knife and systematically applied it during the different film formation phases.³⁶ This allowed accelerating the solvent evaporation starting from the moment of nitrogen blowing. The accelerated timings of the film formation steps and the formation of a stronger perovskite signal were monitored again by in situ absorption measurements. They calculated the first derivative of the measured absorption dA/dt at 500 nm, (i.e. at a wavelength at which the perovskite absorbs) for the natural drying case and for the case when the air knife starts after 40 s (i.e. during the solution phase) (Figure 5b). This derivative qualitatively reflects the perovskite growth rate, which increased by two orders of magnitude upon applying the air knife (Figure 5b). In addition, Hu et al. compared the calculated dA/dt with the expectation of the evolution of perovskite concentration in the framework of a LaMer model to understand the nucleation and growth dynamics with different, growth rate dependent supersaturation scenarios (Figure 5b). Based on this understanding of the in situ absorption data, it finally was possible to adjust and optimize process parameters to obtain high quality perovskite thin films, leading to perovskite solar cells with efficiencies > 20 %.³⁶

Suchan et al. recently investigated the nucleation and growth of MAPbl_{3-x}Cl_x during annealing at different temperatures.³⁸ They considered the temporal evolution of perovskite absorption, which was extracted from *in situ* transflectance measurements (Section 3) during annealing. For all investigated annealing temperatures, resulting time dependent absorption showed a sigmoidal increase (Figure 5c), which they analyzed in the framework of a modified Johnson-Mehl-Avrami-Kolmogorow (JMAK) model for a nucleation and growth process.



Figure 5: (a) 2D Map of the temporal evolution of *in situ* UV–vis absorption during drying of a blade coated perovskite film (top), together with corresponding absorbance evolution at 500 and 700 (bottom). Based on the optical spectra, solutionintermediate- and solid-state could be identified. (b) First derivative of the evolution of absorbance at 500 nm in case for natural drying (black) and air knife blowing (red), starting after 40 s of processing (left). Also shown is an illustration of the temporal evolution of perovskite concentration in the framework of a classical LaMer model in case of nitrogen blowing during solution state (red line), intermediate state (blue), or in case of natural drying (black) (right). (a,b) Reprinted with permission from ref. 36. Copyright 2019, WILEY-VCH. (c) Temporal evolution of MAPbl_{3x-1}Cl_x concentration during annealing at different temperatures, together with fits using a JMAK model with (solid lines) and without (dashed lines) considering a delay time t_{onset} (left). Reprinted with permission from ref. 38. Published by the Royal Society of Chemistry. (d) Temporal evolution of PL peak position and PL intensity during annealing of MAPbl₃ using Pbl₂ (top) or PbCl₂ (bottom) precursors. The shaded areas illustrate ΔE , which is defined as the difference of initial and final PL energy values. Also shown are corresponding 2D maps within the first 20 s of annealing (right). Reprinted with permission from ref. 37. Copyright 2019, WILEY-VCH.

In this model the temporal evolution of the perovskite concentration c(t) is described as

$$c(t) = 1 - e^{-\left(k_0 e^{-\frac{E_a^F}{RT}(t - t_{onset})}\right)^n} \text{ for } t > t_{onset}$$
(6)

With k_0 representing the rate constant, n corresponds to the dimensionality of the growth, E_a^F is the activation energy of the MAPbl_{3-x}Cl_x formation and t_{onset} is a delay time. Only when taking into account t_{onset} in the JMAK model, it was possible to fit the evolution of perovskite absorption for all investigated temperatures, allowing to quantify $E_a^F = (94 \pm 2) kJ mol^{-1}$ as well as an activation energy of the delay time $E_a^O = (84 \pm 7) kJ mol^{-1}$ (Figure 5c). Furthermore, an exponent of $n = 2.1 \pm 0.1$ indicated a 2-dimensional growth of the perovskite.³⁸

Recently, Song et al. investigated the crystallization of MAPbl₃ during spin coating from solution and during subsequent annealing for different lead precursors.³⁷ Here *in situ* PL monitored the film formation and the measured spectra were analyzed by fitting a Gaussian function to the PL peak. This allowed to extract the PL peak position, full width at half maximum (FWHM) and PL intensity as a function of annealing time (Figure 5d). For all lead precursors used, the authors observed an initial appearance of PL, located at higher photon energies than typical bulk PL. The peak shifts to lower energies within the first few seconds, accompanied by a reduction of FWHM. As described in Section 2, both optical signatures indicate a confinement effect, so that the initial PL dynamics can be associated with the growth of perovskite nuclei. For the PbCl₂ precursor, i.e. in case of crystallization of MAPbl₃. xCl_x , PL disappears after the fast initial redshift and reappears only after a certain delay time (Figure 5d). A disappearance of optical features of MAPbl_{3-x}Cl_x in an intermediate time range is in line with the above-described results from Suchan et al..³⁸

From the works presented in this section it becomes clear that monitoring single optical properties *in situ* during processing already allows to gain important insights into the perovskite film formation. This includes accessing nucleation and growth dynamics, or identifying the initial perovskite growth by exploiting PL quantum confinement effects. However, to gain an even more complete picture of perovskite formation, it is necessary to access additional optoelectronic properties. This for example is possible by simultaneous measurements of several optical signals such as PL and Absorption/Reflection, which is the topic of the following section.

4.3. Understanding perovskite film formation based on simultaneous monitoring of multiple optical signals

When measuring different optical quantities simultaneously, it is possible to extract considerably more insight about the perovskite formation than when considering only one component. Despite this fact investigations of the film formation dynamics of halide perovskites by multiple, simultaneously measured optical properties are still rare.

Suchan et al. investigated the spin coating and thermal annealing of the chlorine derived synthesis of MAPbl_{3-x}Cl_x by *in situ* transflectance and PL measurements (Figure 6a), which are supported by XRD and XRF measurements.³⁸ The absorption was extracted from the transflection data *R*, assuming spectrally constant reflection R_0 at the perovskite air interface and full reflection at the bottom of the mirrored substrate, i.e.

$$R(\lambda, t) = R_0(t) + R_1(t) \exp(-\alpha(\lambda, t) 2dc(t)),$$
(7)

where R_1 is a constant, α is the absorption coefficient of the perovskite, d is the overall film thickness, which is assumed to be constant and c is the relative concentration of the perovskite. The spectral dependence of the absorption coefficient was approximated by a direct band-to-band absorption with band gap E_g in combination with Urbach tail absorption with the Urbach energy E_u , yielding

$$\alpha(E) = \begin{cases} \alpha_0 \sqrt{E - E_g} & \text{for } E > E_g + E_u/2\\ \alpha_0 \sqrt{\frac{E_u}{2e}} \exp\left(\frac{E - E_g}{E_u}\right) & \text{for } E < E_g + E_u/2 \end{cases}$$
(8)

Here the upper branch describes the band-to-band absorption, while the lower branch represents the exponential Urbach tail absorption. Figure 6b shows a fit of the measured transflectance data using Equations 7,8. While the applicability of the model well below the band gap might be limited as discussed in Section 2, it allows to determine the concentration of perovskite phase c(t), as evidenced by a good agreement of c(t) determined by *ex situ* XRD and *in situ* transflectance data. As described before, when analyzing c(t), Suchan et al. observed that the MAPbI_{3-x}Cl_x crystallization during annealing was delayed, i.e. starting only after a certain time t_{onset} (Figure 5c), presumably due to the presence of excess chloride.³⁸



Figure 6: (a) *In situ* PL and absorption during the processing of a MAPbI_{3-x}Cl_x film. (b) Fit of Equation 7 to a transflectance spectrum. (c) PLQY (top), calculated implied V_{oc} (top middle), measured PL lifetimes (bottom middle) and calculated relative change in doping density as a function of annealing time. (a-c) Reprinted with permission from ref. 38. Published by the Royal Society of Chemistry.

In corresponding PL data (Figure 6a), the delayed MAPbI_{3-x}Cl_x crystallization is reflected by a significant increase of PL intensity and PLQY after t_{onset} (here after ~40 s). During spin coating (t < 0 s range) and at early annealing times, a clear PL feature was observable, which significantly dropped in intensity upon further annealing until t_{onset} . At the same time, the PL peak shifted to lower energies, which was associated with halide exchange in MAPbI_{3-x}Cl_x towards a higher iodine concentration. The PL results from Suchan et al. deviate to some extend from the PL results for MAPbI_{3-x}Cl_x by Song et al. (Figure 5d) in so far that Song et al. observed complete PL quenching until t_{onset} .³⁷ This could be due to differences in the exact processing and measurement conditions, which were attributed in literature to lead to different MAPbI_{3-x}Cl_x crystallization behaviors.³⁸

Suchan et al. were able to quantify the time dependent absolute PL intensity, which, together with the transflectance data, allowed calculating the PLQY and in turn, the implied V_{oc} during annealing, by using an equation similar to Equation 3. In the course of annealing, the PLQY as well as implied V_{oc} increased, reached a maximum, and then decreased again (Figure 6c). The implied V_{oc} peaked after 38 min of annealing (i.e. even before the PLQY), when only about 30% of the perovskite had formed. To investigate the decrease of PLQY and implied V_{oc} in more detail, time resolved PL at different annealing times was measured. Considering corresponding PLQY values, they could calculate the relative change of doping density according to $PLQY \propto \tau n_0 a_e$, where τ is the minority carrier lifetime, n_0 is the net doping density and a_e is the absorptivity at the emission wavelength (Figure 6c). It turned out that the calculated doping density decreased, which they associated to the decrease of implied V_{oc} .

We recently investigated the two-step processing of MAPbl₃ with spin coating, using the optical detection system and the spin coater described in Section 3 (Figure 3a,e).³⁹⁻⁴⁰ We monitored *in situ* the evolution of optical properties during the second processing step, i.e. starting when MAI dissolved in isopropanol is dripped onto a Pbl₂ thin film that was produced in a prior, first processing step (Figure 7a). Based on the measured PL and absorption within the first 22 s of spin coating (Figure 7b), the film formation process of MAPbl₃ could be divided into five different time ranges.

While no clear absorption was detected directly after dripping MAI/IPA solution, a PL signal was already present, appearing at higher photon energies compared to typical MAPbI₃ bulk values (Figure 7c top). This PL shifted rapidly towards lower energies within the first second of spin coating. We associated the blue shifted PL to stem from a quantum confinement effect, similar to Song et al. in Section 4.2. Using the dependency of the PL peak position on the crystal size (see Equation 5 and Figure 2e), we quantified the temporal growth of MAPbI₃ crystals in Time Range I (Figure 7d). After 1.5 s the crystal size reached values of approx. 20 nm, connecting well to the film thicknesses after approx. 4 seconds, which were calculated from the absorption measurements using Beer Lambert law

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(Figure 7d). This match suggested that a MAPbI₃ layer, monocrystalline in vertical direction formed during Time Range I. In Time Range II, this compact MAPbI₃ layer prevents further MAI diffusion into the now buried PbI₂ layer, thus acting as a capping layer, which was concluded from the temporally constant PL and absorption spectra.



Figure 7: (a) Illustration of the MAPbl₃ two step processing, with *in situ* monitoring of PL and absorption during the second processing step. (b) 2D Maps of the evolution of absorption (top) and normalized PL (bottom) during spin coating. (c) Evolution of PL spectra during processing in Time Range I+II (top), Time Range III (middle) and Time Range (IV) bottom). Corresponding origin for the different PL shifts are indicated at the right. (d) Evolution of film thickness during spin-coating derived with different approaches, that is by converting OD into thickness (black), by exploiting thin film interference (orange diamonds), by association with a confinement effect (red squares) and by associating the PL shift with self-absorption (green triangles). (a-d) Reprinted with permission from ref. 39. Copyright 2020, Royal Society of Chemistry.

In Time Range III, a narrowing of the PL on the high-energy edge was observed (Figure 7c middle). To better understand this PL dynamic, we modelled the spectra using a simple optical model, which considers extended optical paths within the perovskite due to internal reflections at the interface to adjacent media.^{68, 78} It turned out that an increase of perovskite layer thickness to about 500 nm during

Time Range III would be necessary to model the experimentally observed PL shift, in order to attribute it to self-absorption. This was in clear contradiction to the layer thicknesses extracted by absorption, which were about one order of magnitude lower (see Figure 7d between 9.1 s and 12.6 s). However, the difference spectrum (grey area in Figure 7c middle) between the PL at the beginning and the end of Time Range III matched well the PL spectrum at 0 s, allowing to associate the difference PL to PL from still nanoconfined grains in the capping layer. A shift of the difference spectrum in the course of Time Range III towards lower energies would indicate a growth of the nanoconfined grains, but this was not observed. Rather, the difference spectrum maintained its spectral shape and position during Time Range III, while its relative intensity decreased. Thus, detailed PL analysis and simultaneous consideration of absorption allowed to exclude a significant self-absorption effect as well as the growth of nanoconfined grains during Time Range III. In fact, it enabled to identify the beginning of a dissolution process of nanoconfined grains in the capping layer. This is consistent with a dissolutionrecrystallization reaction, which was suggested in literature to occur in the course of perovskite twostep processing.¹¹¹⁻¹¹² Here the dissolution of MAPbl₃ is enabled by an increasing iodine concentration in the MAI/IPA droplet upon solvent evaporation. In Time Range IV the reaction then shifts intensively to the recrystallization process, resulting in a strong increase of perovskite layer thickness, extracted from the absorption data (Figure 7d). In Time Range IV, it was indeed possible to fit the shifting PL using the optical model mentioned above. Here the perovskite layer thicknesses extracted from the PL modelling in Time Range IV matched very well with the thicknesses determined from absorption, which allowed to attribute the PL change in Time Range IV to an increasing self-absorption effect. Thus, it was possible to access the temporal evolution of the layer thickness, during the entire film formation process by analyzing the different optical quantities in detail (Figure 7d). This finally allowed to quantify the growth rates of the perovskite crystallization steps from the slopes in Figure 7d, where a high rate of 445 nm/s of the recrystallization process in Time Range IV pointed towards its crucial role in the film formation dynamics.³⁹

Very recently, simultaneous PL and absorption spectroscopy was used to in situ monitor the formation of mixed perovskite (FAPbI₃)_{0.875}(CsPbBr₃)_{0.125} during spin coating.⁹⁶ Together with considering the layer thicknesses of the final films, the evolution of PL peak position, PL peak width and energetic position of the absorption edge could be extracted as a function of layer thickness. A simultaneous decrease of all three optical parameters indicated the presence of a confinement effect at early processing times. For longer times and subsequently for higher layer thicknesses, PL Peak position and energetic position of the absorption edge further decreased, while the PL peak width remained constant. Such a behavior was attributed to a change in stoichiometry, suggesting a more Cs and Br rich stoichiometry at early spin coating times followed by more pronounced incorporation of FA and I at longer times.⁹⁶

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From the discussed works in this section, it thus becomes clear that considering two or even more optical signal simultaneously during the perovskite processing, allows to extract more information compared to when having only single optical signals, so that deep insights about the occurring film formation dynamics can be gained.

5. Conclusion and Future Prospects

This perspective, highlights recent developments in the field of *in situ* monitoring the film formation process of halide perovskites using optical spectroscopy. It becomes clear that *in situ* optical spectroscopy allows investigating the perovskite film formation at different levels of detail, depending on the individual aims and needs. This starts with the direct consideration of the measured data such as PL- or absorption intensity to quantify the timings of film formation steps, and can extend to the access parameters, which are calculated on the basis of detailed analysis of the measured in situ data. These parameters even allow to access the evolution of the potential optoelectronic functionality of the perovskite during processing such as the implied *V*_{oc}. Furthermore, *in situ* optical spectroscopy enables enhanced process control not only for lab relevant processing methods such as spin coating, but also for solution-based methods that allow for easy upscaling such as blade coating. The basis for this is the technical development of the last years, which improved and facilitated the accessibility of *in situ* optical spectroscopy. This is likely to be beneficial for the entire halide perovskite community, be it for simple monitoring of timings or for complex multimodal measurements e.g. at beam lines, to gain more in-depth insight about the perovskite film formation.

Regarding the investigated material systems so far, mainly the model halide perovskite MAPbl₃ was the focus of interest. This is fair enough, as the crystallization behavior of such a ternary perovskite appears to be well suited to investigate basic crystallization concepts, or to developed *in situ* techniques. However, more complex multinary halide perovskites are more relevant for efficient perovskite based optoelectronic devices, making investigating their film formation process by optical spectroscopy an important future topic. Here we expect that the additional insight provided from detailed analysis of the data will be increasingly relevant, e.g. to clearly differentiate a change of perovskite stoichiometry during processing from other effects such as PL quantum confinement or changes in microstrain of the perovskite.

The latter aspect has to the best of our knowledge not yet been explicitly considered in the analysis of in situ PL data during film formation, even though it is known that changes in microstrain affect the perovskite optical properties. It also has become apparent that microstrain can significantly impact the optoelectronic properties of a perovskite layer,¹¹³making it feasible that changes in strain also occur during film formation. Due to the possibility to differentiate the optical signatures of changes in strain from other effects such as quantum confinement (Section 2), especially in situ PL spectroscopy could become a valuable method to investigate epitaxial growth of perovskites in the future.¹¹⁴ It could also be used to facilitate targeted stabilization and strain management of perovskite structures and interfaces in optoelectronic devices.^{96, 115}

Another future aspect of optical *in situ* spectroscopy becomes obvious when considering that so far only the formation of the perovskite has been investigated, but little attention has been paid to investigate solvent states and intermediate complex states during film formation by optical *in situ* spectroscopy. It is known that already in the precursor solution, e.g. depending on the iodine concentration and solvent, different iodoplumbate complexes such as Pbl₃⁻ or Pbl₄²⁻ can form, which show clear absorption signatures in the UV range.¹¹⁶⁻¹¹⁷ The further perovskite crystallization was found to strongly depend on these precursor states, ¹¹⁸⁻¹¹⁹ making it important to study and understand the dynamics of these solution states during perovskite processing. This is especially important for solvent mixtures as they are often used in state-of-the-art perovskite solution processing. Here, predominantly *in situ* absorption with a sufficient time resolution could be an attractive characterization method to directly investigate the transformation from precursor solution to perovskite during solution processing.

Also, when it comes to the perovskite crystallization, there is still potential to gain a more fundamental understanding with the help of optical in situ spectroscopy. In particular, the formation of intermediate phases or the formation of crystalline perovskite solvent complexes often play an important role for the film formation process, where e.g. needle-like structures can form.^{19-20, 120-123}However, these features have so far been studied mainly using scattering techniques,^{19, 21, 24} while only a few studies used optical *in situ* spectroscopy.¹²⁴ One reason for this could be that these crystalline structures are often optically inactive and have a rather transparent appearance, preventing measurement of intense and clear PL or absorption signatures. During the film formation process, solvent complex structures often exist on length scales comparable to the wavelength range of typical light sources used for the spectroscopic investigations. This circumstance could be used to utilize the optical scattering expected at the solvent complexes, to indirectly characterize the crystallization dynamics and also the transformation of the complex structures to pure perovskites. This could be measured e.g. with the help of *in situ* reflection spectroscopy, but also when measuring *in situ* transmission spectra, optical scattering at solvent complex phases would become noticeable by a baseline lift in the optical density.

Finally, it can be noted that the available optical data that is obtained, and possibly even already processed, in the course of film formation may allow for a significant advance, if not even a paradigm

shift, in the preparation of halide perovskite-based devices. It allows moving from a rigid processing protocol (that was retrospectively obtained from previous measurements) with set timings for each step, to a process control that relies on the evolution of optical signatures. In combination with high throughput methods such as automatized and autonomous setups including KI supported data analysis, optical *in situ* measurements during perovskite formation could evolve as a substantial building stone to impel the commercialization of perovskite based optoelectronic devices in the future.

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Biographies



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Fabian Panzer is Habilitation candidate and leads the perovskite subgroup within the Soft Matter Optoelectronics group at the University of Bayreuth. He completed his Diploma in Physics in 2013 at the University of Bayreuth, where he also obtained his Ph.D in 2016. His research focuses on understanding the processing of emerging semiconductors such as halide perovskites or organic semiconductors, for application in optoelectronic devices like solar cells or X-ray detectors.

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