Abstract

Metal halide perovskites have shown much promise for the next generation of photovoltaic solar cells. One problem hindering the widespread use is the limited stability of the material. In this work micro photoluminescence spectroscopy is used to study degradation of perovskite solar cells in ambient conditions. This is done by using the generalized Planck equation to calculate the band-to-band absorptance spectrum. Results show that it is possible to accurately find the band-to-band absorptance in the sub band gap domain. By repeating the mapping over time the change in absorptance over time can be derived. The results show that when exposed to ambient conditions, the PL peak red-shifts, the band gap energy decreases and sub band gap band-to-band absorption increases. This change is likely due to phase segregation induced by moisture.

The PL signal intensity increases for some samples over time and decreases for others. It is shown that two processes compete, an increase in luminescence caused by the excitation laser and a decrease caused by degradation. These two competing processes, one of which caused by the measurement method, makes measurement of the PL intensity an inaccurate method of measuring degradation of perovskite solar cells. The method suggested in this work is less affected by the laser light and is a more accurate and versatile method of measuring degradation than measuring luminescence intensity.
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1 INTRODUCTION

Metal halide perovskites are a group of organic-inorganic materials with the basic composition of ABX$_3$ with A a cation, such as methylammonium (MA), formamidinium (FA), rubidium or cesium, B tin or lead and X a halide ion, either iodide, bromide or chloride. The most commonly used metal halide perovskite material is MAPbI$_3$.

Metal halide perovskite materials have shown much potential for next generation photovoltaic solar cells. It has several advantages over other materials such as a direct band gap, a high absorption coefficient and a low recombination rate, leading to high quantum efficiencies and perovskites can be deposited with cost effective solvent methods.

The efficiency of perovskite solar cells (PSC) has increased rapidly in the last decade, from 3.8 % in 2009 to 24.2 % in 2019. There is also a lot of potential for perovskite to be used in tandem configurations with silicon or another perovskite material. Tandem perovskite-silicon cells have reached efficiencies of 28.1 %, higher than single junction silicon cells.

One of the factors hindering wide spread adoption is limited stability of PSCs. Light, oxygen, temperature, humidity, electric fields and more can all induce degradation in PSCs. In order to improve stability the cells can be enclosed, and research groups have also used different material compositions to improve the intrinsic stability of the material. Instead of using MAPbI$_3$, different combinations of cations and halides can be used. By using a mixture of iodide and bromide as halides the band gap of the material can be tuned and it leads to better performance. Using multiple cations superior performance and stability has been reported. Such as by using a quadruple cation mixture with MA, FA, rubidium and cesium. In this work a quadruple cation mixed halide perovskite Cs$_{0.07}$Rb$_{0.03}$FA$_{0.765}$MA$_{0.135}$PbI$_{2.55}$Br$_{0.45}$ is used. A compact indium doped TiO$_2$ layer and a mesoporous TiO$_2$ layer is used as electron transport layer and Spiro-OMeTAD as hole transport layer. In order to improve non-radiative recombination on the perovskite-TiO$_2$ interface a thin layer of a Phenyl-C61-butyric acid methyl ester (PCBM) and Poly(methyl methacrylate) (PMMA) mixture is used as a passivation layer. This also reduces hysteresis in the JV measurements. This state of the art architecture gives superior performance with over 20 % efficiency. More detail on the architecture can be found in the work of Peng et al.

In this work I suggest a novel approach to measure degradation processes in PSCs using micro photoluminescence mapping. Luminescence mapping detects light emitted from recombining electron-hole pairs. These carriers can be generated using an external light source (photoluminescence/PL) or by applying an electric bias (electroluminescence/EL). The emitted light can be detected with a charge coupled device (CCD) detector. The light can be spatially resolved to generate a 2D optical image of the PL or EL intensity, or the light can be spectrally resolved with a grating to generate a spectrum of the light.

Spatial PL/EL imaging is heavily used as a characterization technique for silicon photovoltaics. For perovskite materials this technique is also increasingly used for characterization. Various parameters can be spatially defined such as implied open circuit voltage and series resistance.

From spectrally resolved PL/EL the temperature, band gap and absorption coefficient can be derived. In this work the PL spectrum is measured with a confocal microscope setup. This setup can measure PL on a micron scale and is therefore referred to as a micro photoluminescence setup. The stage is movable in three dimensions, so it is possible to make 2D hyperspectral maps.

The generalized Planck equation is used to calculate the band-to-band absorptance spectra. With this method it is possible to find the low absorption coefficients for sub band gap absorption. This method has been used for silicon and perovskite. By repeating this mapping process every 60 minutes changes over time can be measured. I will use this to investigate changes in the absorp-
tance spectrum over space and time to characterize degradation of PSCs.
2 THEORY

The rate of spontaneous emission ($r_{sp}$) by a semiconductor is given by the generalized Planck equation [17,18]. For the emission of a solid angle of $4\pi$ this gives

$$r_{sp} = \alpha_{bb}(\hbar\omega) \cdot \frac{n^2(\hbar\omega)^2}{\pi^2\hbar^3c^2} \cdot \frac{1}{\exp\left(\frac{\hbar\omega - \mu_\gamma}{kT}\right) - 1}$$

with $\alpha_{bb}$ the band-to-band absorption coefficient, $n$ the refractive index, $\hbar$ the reduced Planck constant, $\omega$ the angular frequency, $c$ the speed of light, $\mu_\gamma$ the chemical potential for photons, $k$ the Boltzmann constant and $T$ the temperature.

The chemical potential for photons $\mu_\gamma$ is equal to the quasi Fermi level splitting which is also equal to the implied open circuit voltage multiplied with the elementary charge. For a solar cell in one sun illumination the maximum value of $\mu_\gamma$ is given by the Shockley and Queisser limit [19]. In this limit all generated carrier recombine radiatively. Non-radiative recombination reduces the chemical potential and thus $r_{sp}$.

The emitted photon current density $d_{je}$ of a uniform planar layer of semiconductor material with a certain thickness is given by [20]

$$d_{je} = [1 - R(\hbar\omega)] \cdot \frac{A_{bb}(\hbar\omega) \cdot (\hbar\omega)^2}{\pi^2\hbar^3c^2} \cdot \frac{1}{\exp\left(\frac{\hbar\omega - \mu_\gamma}{kT}\right) - 1}$$

with $R(\hbar\omega)$ the reflectivity of the perovskite surface, and $A_{bb}$ the band-to-band absorptance of the sample. The emitted photon current density can be measured with the micro-PL setup. The absorptance is the fraction of incident light that is reflected. Equation 2 can be simplified using the fact that $\hbar\omega - \mu_\gamma \gg kT$. In this work I am not interested in the absolute value of the absorptance but the wavelength dependency of the absorptance. This further simplifies the equation to [16]

$$d_{je} \propto A_{bb}(\hbar\omega) \cdot (\hbar\omega)^2 \exp\left(\frac{-\hbar\omega}{kT}\right)$$

where $d_{je}$ is proportional to the measured signal. The temperature is not equal to ambient temperature, the high laser intensity increases the temperature. The method of finding the temperature is explained later in this work.
3 EXPERIMENTATION

3.1 CELL FABRICATION

The manufacturing process mainly consists of spin coating deposition. The solutions where prepared as described in the work by Peng et al. [9], this work also contains more in depth information on the manufacturing process. A layer of In-TiO$_x$ of 70 nm is deposited on a cleaned ITO glass substrate by spin coating. This is sintered at 500°C for 30 minutes. A 110 nm mesoporous layer of TiO$_2$ is deposited using spin coating followed by the ultra thin PMMA:PCBM layer which is also deposited using spin coating. The sample is annealed at 100°C for 10 minutes. The perovskite layer is then deposited in a one step process by spin coating. The substrate is then annealed again at 100°C for 45 minutes. The Spiro-OMeTAD is deposited using spin coating. The process is finalized by depositing 100 nm of gold using shadow masking.

3.2 MICRO-PL

The micro photoluminescence spectra were acquired using a Horiba LabRam HR Evolution confocal microscope setup with an excitation laser at 532 nm with a power of 20 mW which is attenuated to 2 µW using neutral density filters. The emission hole diameter was set to 500 µm, large enough that all light is collected. A 10x zoom 0.25 NA objective was used which lead to a diffraction limited spot size of 2.6 µm in diameter. This gives an average laser power of 18.9 W/cm$^2$ which is approximately 190 suns. The sample is placed in a temperature and atmosphere controlled enclosure on an XYZ movable stage. A grating separates the acquired PL signal and the signal is measured on a 1024 pixel Syncerity EO silicon charge coupled detector (CCD) with a spectral resolution of $\sim$0.21 nm. More information on the micro-PL setup can be found in [21].

3.3 SPECTROPHOTOMETER

A PelkinElmer Lambda 1050 spectrophotometer with integrating sphere setup was used to measure reflectance and transmission characteristics of cells and films. The measurements were calibrated with a calibrated Spectralon coated sample. The measurements were performed from 650 to 850 nm with a 1 nm step size and an acquisition time of 0.8 s per step.

3.4 SOLAR SIMULATOR

JV curves were measured using a xenon light source Photo Emission Tech SS150 solar simulator. Results were analyzed using a Autolab PGSTAT204 galvanostat/potentiotstat. The samples were light soaked for 10 s and then scanned from 1.2 V to -0.05 V (reverse) and then immediately from -0.05 V to 1.2 V (forward) both with a scan speed of 50 mV/s. No mask was used, and the active area of the cell was defined by the area of the gold contact at 0.165 cm$^2$.
Figure 1: a) The PL spectrum for different laser intensities. A 10x10 mapping was made of the sample for each of the intensities at the same location, which were averaged and then normalized. The spectra are almost identical meaning that free carrier absorption is negligible. b) EL spectra for different forward biases and the PL spectrum for the same location. The spectra are normalized. The similar shape indicates that carrier/photon smearing has a negligible effect on the measurements. c) The measured PL signal is compared to $d_j$ calculated from $A_{tot}$ at different temperatures. The values are normalized at 1.65 eV. The graph shows that the best fit is achieved for 320 K.

4 RESULTS

In order to validate equation 3, three different tests are performed. The first is to test if free carrier absorption can be neglected, the second test is to see if carrier/photon smearing has an impact, and third, the absorptance derived from PL is compared to absorptance as measured by spectrophotometer.

4.1 FREE CARRIER ABSORPTION

Apart from band-to-band absorption, photons can also be absorbed by free-carrier absorption. If free carrier absorption is a big fraction of the total absorption, equation 3 no longer holds. The free carrier absorption coefficient is dependent on the free carrier density, so to test if free carrier absorption has an influence on the measurements, the PL spectrum is measured with different excitation powers. If the spectra are identical in shape, this means that free carrier absorption has a negligible effect on the performed measurements. Figure 1a shows the results of this test. The fact that the spectra are almost identical shows that free carrier absorption has a negligible effect on the measurements.

4.2 CARRIER/PHOTON SMEARING

The focused laser of the micro-PL setup excites a small area. Free carriers and photons exit the excitation area, in a process called carrier/photon smearing and interact with the material outside this area and emitting photons. As the area from which emitted photons are detected is larger than the excitation area, these photons are also detected. The photons emitted from outside the excited area originate from
different circumstances so could alter the measured spectrum. In order to test if carrier/photon smearing has a significant effect on the measurements, the EL spectrum is compared to the PL spectrum. EL causes emission from the whole of the active area of the cell, so the carrier and photon densities are more uniform, meaning that carrier/photon smearing does not occur. If the EL spectra are similar to PL spectra, then it can be concluded that carrier/photon smearing has a negligible effect on the measured PL spectra. A forward bias is applied to the terminals of the cell and for different voltages the EL spectrum is measured. The EL spectra compared to the PL spectrum from the same spot are shown in figure[1]. Similarity between the spectra indicates that carrier/photon smearing has a negligible effect on the measurements.

4.3 SPECTROPHOTOMETER

Absorptance measured by the integrating sphere spectrophotometer is given by

\[ A_{\text{tot}} = 1 - R - T \]  
(4)

with \( A_{\text{tot}} \) the total absorptance, \( R \) the measured reflectance and \( T \) the measured transmittance of the sample. For an assembled cell with a gold back contact the transmission \( T \) is equal to zero.

Using equation (3) \( J_\text{e} \) can be calculated from the measured absorptance \( A_{\text{tot}} \). To find the temperature the measured and calculated values of \( J_\text{e} \) are plotted for different temperatures in figure [1]. The curves are normalized at the value of 1.65 eV. This shows that the best fit is given for a temperature of 320 K, which is higher than room temperature. This could be due to heating of the sample by the laser light and other groups have reported similar heating [22, 23].

Using the temperature of 320 K \( A_{\text{bb}} \) can be calculated from the measured PL signal. The calculated value of \( A_{\text{bb}} \) is normalized to the measured absorptance \( A_{\text{tot}} \) in the range of 720-730 nm. In figure [2], \( A_{\text{tot}} \) is compared to \( A_{\text{bb}} \) for a perovskite film that is deposited on an ITO layer on top of a glass substrate. For low energies \( A_{\text{tot}} \) is higher than \( A_{\text{bb}} \). If \( A_{\text{tot}} \) is compared to the measured absorptance of a glass substrate coated with ITO, it appears that the difference is due to parasitic absorption of the ITO and glass.

For an assembled cell the \( A_{\text{bb}} \) and \( A_{\text{tot}} \) are plotted in figure [3]. Sub band gap \( A_{\text{tot}} \) is higher than \( A_{\text{bb}} \), similar to the perovskite film. This likely due to parasitic absorption of the transport layers. This also shows that it is not possible to use a spectrophotometer to accurately measure sub band gap absorptance for assembled cells. The absorptance derived from the PL signal can be measured to values as low as \( 10^{-6} \) with the settings used in this work and Barugkin et al. have used this method to find absorption coefficients of perovskite as low as \( 10^{-14} \text{cm}^{-1} \) [16]. Accuracy of the spectrophotometer is limited to a few percent.

In order to calculate the absorptance from the micro-PL quantitatively it has to be normalized to a known absorptance at a known wavelength. Measurements with the spectrophotometer have shown that the absorptance above the band gap in the range of 720 to 730 nm is uniform over the sample, and stays constant over time (figure [2c]) at 85.6 %. For each measurement \( A_{\text{bb}} \) is normalized to 0.856 in the range of 720 to 730 nm.

4.4 MICRO-PL MEASUREMENTS

With the micro-PL setup the size of the scanned area and resolution can be set to what is required. It is both possible to look at micro scale images with a resolution of a few microns or at the whole of the cell. Scan times go up with higher pixel counts, a 100x100 map takes approximately 40 minutes with the used
Figure 2: a) The calculated absorptance and the measured absorptance of a perovskite film on ITO and glass and absorptance of just ITO and glass. Parasitic absorption of ITO and glass dominates the sub band gap absorptance. b) The calculated absorptance and the measured absorptance for a complete cell. The transport layers dominate sub band gap absorptance. c) The above band gap absorptance between 720 nm and 730 nm of a complete cell stays constant when exposed to air for 48 hours. Note that the old sample is red-shifted. This is explained in more detail in section 4.6.

The used resolution was 101x101 pixels with a scanned area of around 4500x4500 \( \mu m \), large enough to fit the whole cell area. The measurements can be automated to run at a predefined time interval, this makes it possible to measure how the material changes over time. In the next sections the sample was exposed to ambient air at a temperature of 20 \( \pm \) 1°C at 35 \( \pm \) 5% relative humidity. The micro-PL measurements were repeated every hour.

4.5 Signal intensity

Figure 3: X-Y map of the maximum value of a PSC at a) t=0h, b) t=8h and c) t=42h. Some Heterogeneity is visible in the sample at t=0h and t=8h.
Degradation measurements were performed on three different samples (6D, 6H, and 8A) for around 46 hours. Maps for the maximum value of the luminescence peak is shown in figure 3 for sample 8A. The cell averages for each hour are shown in figure 4a. The error bars represent the standard deviation in the distribution of the different pixels. The starting points are normalized to one. Two samples from batch 6 both increase over time, while the sample from batch 8 decreases over time. Since the absorptance and temperature are almost constant, the change in intensity is due to change in $\mu_r$, which means a change in non-radiative recombination. Research has shown that the PL intensity of perovskite can increase when exposed to light [24] on a second to hour timescale. This is due to light induced trap de-activation reducing non-radiative recombination [25]. This process is influenced by gasses in the atmosphere, especially oxygen has a strong influence on trap de-activation [26]. This process is reversible in the dark. The change in luminescence has been reported as high as 10 or 100 fold. This effect can be reproduced in our samples, this is shown in figure 4b. After continuously illuminating our samples for 200 seconds the PL intensity has increased by 130%. In the degradation tests the increase for sample 6A and 6H is limited at around 40%, this can be explained by the short illumination times ($\sim$0.1 s) and long time in the dark ($\sim$1 hour).

A decrease in intensity corresponds to an increase in non-radiative recombination, which can be caused by degradation of the sample. If the sample is stored in dark ambient conditions for 62 hours the PL intensity decreases by around 60%, as can be seen in figure 4c.

It is likely that these two processes compete, on the one hand ambient conditions cause degradation of the sample, increasing non-radiative recombination, thus reducing PL and on the other hand light induced trap de-activation reducing non-radiative recombination and increasing PL. Which process is dominant could be dependent on the quality of the material, in high quality material with a low trap density degradation dominates, while in a low quality material trap de-activation dominates.
Two methods of finding the band gap are compared, using the position of the peak and using a Tauc fit. The methods give similar results. The Urbach tail can be fitted and from this fit the Urbach energy can be calculated.

Band gap over time for different samples, the band gap energy decreases for all samples. Switching the gas supply to the sample shows that change in band gap is reversible. When exposed to dry nitrogen gas the band gap increases. The Tauc plot shows \((\hbar \omega \alpha)^2\) as a function of \(\hbar \omega\) for a fresh perovskite film on ITO glass and the same film after being exposed to ambient conditions for 62 hours. \(\alpha\) is derived from \(A_{tot}\) which is measured by spectrophotometer. The optical band gap decreases, indicating that the decrease in band gap also occurs without micro-PL laser light.

The optical band gap of a material can be found using the Tauc-plot method [27]. \((\hbar \omega \alpha)^2\) is plotted against \(\hbar \omega\) and a straight line is fitted. The x-value of the point where this line intersects the x-axis is the optical band gap energy. The absorption coefficient \(\alpha(\hbar \omega)\) can be derived from the absorptance \(A_{tot}\) and the reflectivity \(R\) by

\[
\alpha(\hbar \omega) \propto -\ln\left(\frac{A_{tot} + R - 1}{A_{tot} \cdot R + R - 1}\right)
\]
which is derived from the function given in the work by Barugkin et al. [16]. In the conducted measurements this value is closely related to the peak value of the PL spectrum. In figure 5a the PL signal location is compared to the Tauc-plot for a perovskite film and the values are almost identical. However using the peak location is more robust and less computationally intensive as it does not require fitting. So for the rest of this work if the optical band gap is mentioned this is defined as the peak position of the PL signal.

The optical band gap energy decreases over time for all samples when exposed to ambient conditions as shown in figure 6a. To confirm that the change in band gap is due to an exposure to ambient conditions, a test was performed, for the first 21 hours the sample was exposed to ambient air, then the gas in the measurement chamber was changed to dry nitrogen for 21 hours and then the gas was changed back to ambient air for 21 hours. The results of this are shown in figure 6b and show that the optical band gap only decreases in ambient conditions and increases when exposed to dry nitrogen. This means that the change in band gap is in fact due to atmospheric conditions. In order to exclude the effect of the laser on the degradation, a perovskite film was deposited on an ITO glass, the absorbance was measured using the spectrophotometer, the sample was then exposed to ambient air for 62 hours and the absorbance was measured again. Using the Tauc-plot method the optical band gap was found to have decreased 3 meV between the two measurements. The Tauc plots are shown in figure 6c.

In literature a decrease in band gap has also been reported in multication and mixed halide perovskites due to phase segregation [28]. In quadruple cation perovskites 12h of exposure to 1 sun in N2 atmosphere caused a decrease in the optical band gap of 74 meV. If the sample is then exposed to the dark for 12 hours the phase shift returns back close to the original band gap [29]. Hu et al. have observed a decrease in band gap after exposure to moisture in quadruple cation mixed halide (RbCsFAMAPbIBr) perovskite films [30]. After a period of 1 hour in 90% relative humidity in the dark the optical band gap decreased by 10 meV. They concluded this change was due to formation of bromine rich and poor phases.

In literature it has also been reported that for MAPb(I\(_x\)Br\(_{1-x}\))\(_3\) phase segregation causes an increase in PL intensity. This is because the low band gap regions have a higher luminescence efficiency than the original material [31]. In my samples however, storage in dark ambient conditions show a decrease in band gap and decrease in luminescence. This indicates that for the quadruple cation mixed halide perovskite that was used the degraded state has a lower luminescence efficiency.

Although phase segregation is a plausible explanation for the observed decrease in the optical band gap I have not been able to directly show this in the samples.

4.7 Urbach Tail

The absorbance spectrum has a specific form, for energies above the band gap the absorbance is high and near constant, while for photon energies below the band gap the absorbance shows an exponential decay. This sub band gap decay is called the Urbach tail. This tail in absorption was first described for AgBr crystals by Franz Urbach in 1953 [32] and has since then been found for various different materials. This tail is given by

\[
A_{bb,\text{tail}} = c \cdot \exp \left( \frac{\hbar \omega}{E_U} \right)
\]

with \(c\) a fitted variable and \(E_U\) the Urbach energy. The Urbach energy characterizes the disorder in the crystalline lattice [33]. An Urbach tail has been described for perovskites [34] and the Urbach energy has been measured at \(\sim 15\) meV [35].

In figure 5, the Urbach tail and fit is plotted. The Urbach energy has been found to be around 13meV. The Urbach energy stays constant after exposure to ambient conditions with a change less than 0.1 meV in 47 hours.

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4.8 **Absorptance**

**Figure 7:** a) Band-to-band absorptance for different wavelengths. For all wavelengths the absorptance increases and for longer wavelengths this increase is faster. The first point is normalized to one. b) The absorption decreases when exposed to nitrogen showing that the change is affected by the gas composition. c) The absorption is plotted against the distance from the side of the cell for different points in time. The data is generated by averaging all points with a certain distance from the left wall. It shows that the increase in absorptance propagates from the side.

Sub band gap absorptance increases for all wavelengths, and for longer wavelengths this change is faster as can be seen in figure 7a. The absorptance spectrum is dependent on the optical band gap and the Urbach energy. The change in absorptance is attributed to change in band gap as the Urbach energy stays constant. In the rest of this work the absorptance at 800 nm is used as it changes significantly over time with little noise. Figure 7b shows that the increase in band gap can be reversed by exposing the cell to dry nitrogen. This shows that the ambient atmosphere is causing the increase in absorptance.

Maps of the absorptance at 800 nm is shown in figure 8 for different points in time. It shows that the absorptance increases beginning from the sides and certain regions inside the cell. At the end of the measurement the change slows downs and the absorptance is mostly uniform over the sample. Figure 7c shows the absorptance as a function of distance from the sides for different points in time. It shows that the increase in absorptance originates from the sides and that there is a sideways gradient. The gold back contact is impenetrable to oxygen and moisture so the degradation must originate from either the edges of the gold contact, or holes in the gold layer. Oxygen and moisture must then translate sideways through the perovskite and transport layers to reach the rest of the cell. The sideways gradient and increase in absorptance shown in figure 7c is similar to sideways diffusion as given by Fick’s law.

Over time different regions show different behavior. Two regions, A and B are indicated in figure 9a and 9c. Region A is likely a hole in the gold contact. Figure 9d shows that the absorptance in region A increases faster than region B. After a rapid increase the absorptance in region A plateaus. In region B the increase absorptance is slow at first, fastens and slows down again.

The change in PL peak height is shown in figure 9b for the same regions. For region A the sharp increase in absorptance corresponds to a decrease in PL intensity. As the absorptance plateaus, the PL intensity increases. For region B the PL intensity increases at first, and when the absorptance starts increasing faster the PL intensity decreases. This behavior is different than for the average of the cell.
Figure 8: band-to-band absorptance at 800 nm for different times. This shows an increase in absorptance over time, and the increase appears to originate from the edges of the cell and certain regions inside the cell.

both region A and B a fast increase in absorptance corresponds to a decrease in PL intensity, while a slow increase in absorptance corresponds to an increase in PL intensity.

This matches the previously mentioned two competing mechanisms, trap de-activation caused by the excitation laser and phase segregation due to exposure to dark ambient conditions. A fast increase in absorptance corresponds to fast phase segregation which then dominates trap de-activation, leading to an increase in non-radiative recombination, and thus a decrease the PL intensity. For a slow increase in absorptance trap de-activation dominates, thus PL increases.

The performance of a cell was measured using a solar simulator. The cell was exposed to ambient air and the JV curve was measured every 24 hours. Results of these measurements are shown in figure 10 as a function of time. Each consecutive day the performance of the cell decreases in open circuit voltage, short circuit current, fill factor and efficiency. Hysteresis also increases over time. This indicates that the sample is degrading due to exposure to ambient conditions. After 72 hours the short circuit current has decreased to zero. The cell performance as measured by the JV curve is not just dependent on the perovskite layer but also on the transport layers and their interfaces, so the measured decrease can have different origins.
Figure 9: a) Map of the maximum value at t=8h, Region A and B are indicated with the black boxes. b) Change in the maximum value over time for the two regions and the cell average. The regions show different behaviors. c) Map of the band-to-band absorptance at 800 nm, with the same regions indicated as a). d) Change in maximum value over time for the indicated regions and the cell average. Region A shows a faster increase in absorptance than the average and region B shows a slower increase.

Figure 10: Cell performance as measured by solar simulator JV scan.
5 Conclusion

In this work a novel method of analyzing degradation processes for perovskite materials is put forth. By measuring the PL spectrum using the micro-PL setup it is possible to find the band-to-band absorptance spectrum of assembled PSCs using the generalized Planck equation. Experimentation has shown that free carrier absorption and carrier/photon smearing has a negligible effect on the measurements. The calculated band-to-band absorptance was compared to the absorptance measured by spectrophotometer. These results have a mismatch that can be attributed to parasitic absorption of the non-perovskite layers of the devices.

A hyperspectral map was created every 60 minutes and the change in the PL and absorptance spectra over time and space was investigated when exposed to the ambient atmosphere. The results show that the Urbach energy does not change over time. The location of the PL peak red-shifts over time for all samples and this coincides with an increase in sub band gap band-to-band absorptance. In literature phase segregation has shown to cause a decrease in band gap energy. Literature has also shown that phase segregation can be caused by light in a nitrogen atmosphere and by moisture in the dark. PL measurements in nitrogen atmosphere show a blue-shift in band gap and measurements by spectrophotometer of a fresh sample and the same sample aged in ambient atmosphere show a red-shift. It can therefore be concluded that the red-shift measured by micro-PL are caused by exposure to ambient atmosphere and not the laser light of the micro-PL setup. Moisture in the ambient atmosphere is likely the cause, but this has not been tested.

Change in band gap corresponds to a change in absorptance, but there are some distinct advantages of analyzing the band-to-band absorptance compared to just the band gap. First the change in absorptance is significantly bigger than the change in band gap, and there is significantly less noise. Small changes can therefore be measured more accurately. Another advantage is for measuring the absorptance of the two absorbers in silicon-perovskite tandem cells. By measuring the PL signal, the absorptance of the perovskite can be found, but getting the absorptance of silicon using PL is not possible because the signal intensity of silicon is much lower than that of perovskite. Instead the absorptance of silicon can be found as the difference between the band-to-band absorptance as found by PL and the absorptance as found by spectrophotometry. This novel characterization method is explained in detail in an upcoming paper by Nguyen et al.

The PL intensity changes over time, for some samples the intensity increases over time while for other the intensity decreases. The PL intensity is linked to implied open circuit voltage which is related to the rate of non-radiative recombination. It has been shown that two processes compete: light increases luminescence and degradation due to ambient atmosphere decreases luminescence. The measured PL intensity is thus affected by exposure to the laser light, meaning that acquired results of the PL intensity are not indicative of the change in performance in one sun or dark conditions. This work shows that the band gap is not measurably impacted by the laser light and is therefore more representative of degradation processes in dark conditions.

JV curves measured with a solar simulator show that the performance of a perovskite cell decrease over time when exposed to ambient conditions. The open circuit voltage decreases over time, indicating an increase in non-radiative recombination. There is also a decrease in fill factor and short circuit current indicating that the transport layers also degrade, however this cannot be measured by PL. This is one of the disadvantages of the used method. The PL spectrum is only affected by the perovskite layer. Instead of using laser light an external bias can be used. EL will be affected by changes in the transport layers. The disadvantage of this method is that it is unstable over time and causes fast degradation of the sample. An alternative disadvantage of the used technique is that it is slow, mapping time goes up.
linear with resolution. While a CCD camera setup can have a resolution of 1024x1024 pixels and can take a measurement within seconds, the micro-PL setup takes around 40 minutes to take a 100x100 measurement. This makes it less suitable for industrial in-line characterization. Another disadvantage is the high intensity of the laser light. This could potentially be solved by using a larger excitation area of the laser and a larger acquisition area.

In conclusion, this work presents a novel approach to measuring and analyzing degradation processes in PSCs. The change in absorptance can be used to better understand the effects of different gasses to the perovskite in assembled cells. This could be useful for analyzing new material compositions or cell structures. The micro-PL setup can analyze both macro scale and micro scale. This work has focused on the macro scale of the whole cell, but it could be interesting to look at changes on the micro scale. This work also focuses on perovskite, but this method could be used in a similar fashion for different materials.

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7 References


