university of groningen
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# The Effects of Ionic Liquids on Tin Perovskite Solar Cells

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# 1 Abstract

Tin perovskite solar cells are excellent candidates for advanced solar cells given the high absorption coefficient, diffusion length and carrier mobility. However the fast oxidation of tin inside the perovskite together with large quantity of trap states lead to greatly reduced efficiencies for the solar cell. Elimination of the grain boundaries by growing compact tin perovskite films with large grains is one promising strategy to overcome these issues. Several research groups have focused on the addition of ionic liquid (IL) to improve morphology and environmental sensitivity, reporting bigger grains and better stability. All the literature found focuses on improving lead perovskites. Within this study there is IL added to the precursor solution for a tin hybrid perovskite solar cell. There were trials with multiple *-imidizolium* based IL's (see section 4.1), showing similar behaviour within the fabricated device. Increase in the short circuit current is observed, likely due to reduced surface roughness or bigger grains. A negative effect was a decrease in open circuit voltage for higher concentrations of IL, where the ionic liquid EMIMOTF showed less of this effect than the other trialed IL's. This effect can be attributed to more pinholes formed in the material with increasing IL. Although the results were hard to quantify there do seem to be positive effects from adding certain types of IL, be it that for significant improvement the concentration and fabrication needs to be refined.

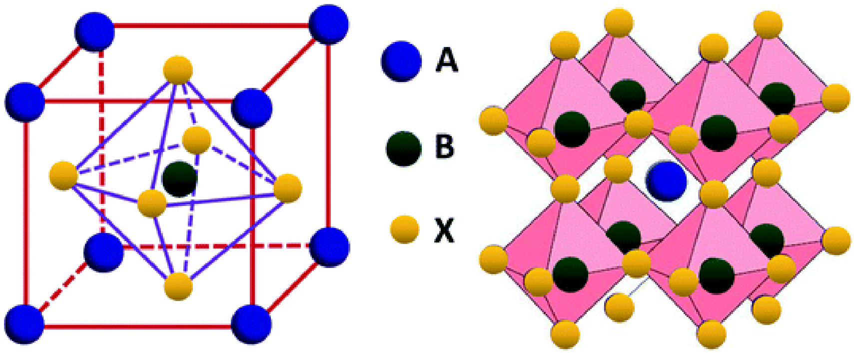
# Contents

# 2 Introduction

Over the last years a lot of research has been conducted regarding metal halide perovskite solar cells(PSC's) with efficiencies reaching 23%[1]. The perovskite structure interacts with light much more than most materials due to high absorption coefficients, which together with good charge carrier mobility, balanced hole and electron transport and tunable band-gap form the ideal properties for a solar cell[2][3]. Also the material is flexible sparking imagination toward new applications for solar cells. 3D Perovskite is the generic name for all compounds with the general formula $ABX_3$, with A and B usually an inorganic cation while X usually being oxygen or halogens[4](See figure 1).

Lead based PSC's have shown the best efficiencies; however because of toxicity to plants and animals[5][6][7] it may have severe environmental implications when used on the large scale. How harmful lead inside the PSC actually is, is still under debate. Because of the uncertainty tin perovskite is investigated, given the low toxicity[8] and respectable theoretical properties. Around the year 2000 it was already in the focus of research but dismissed as good PSC suitor due to low stability and high oxidation[9]. Now there is big motivation for an environmental friendly PSC together with the strict regulations related to lead containing products in the EU, hence the reconsideration. Currently the limiting factor for tin PSC's is the background free carrier density[10]. The origin for these carriers is mostly attributed to $Sn^{2+}$ readily reacting with air to become $Sn^{4+}$, inducing positive doping[11]. Recently, Shao et al. demonstrated that a small quantity of 2D tin perovskite not only reduces the density of the grain boundaries, but also induces highly orientated and crystalline 3D tin perovskite domains, which effectively reduces the tin vacancies and the tin oxidation. As a consequence, the 2D/3D based tin solar cells exhibited much higher efficiency and stability compared to the pure 3D based tin solar cells[12]. effective strategies for improving stability of the tin PSC further would be a surface passivation agent or to somehow grow bigger grains inside the device, leaving less surface area for the tin to react with (mostly) air. Several ideas have been stated, like a mono-layer for the crystal to grow on[13][14], several deposition techniques, a fast insulating oxidizing layer on top of the perovskite[15] and so forth.

Recent studies demonstrated that ionic liquid can be used to passivate the surface and/or control crystal growth of the lead based perovskite[16][17]. First a little background on ionic liquids, which are simply salts in a liquid state with a low melting point and low vapor pressure at room temperature. The first ionic liquid (IL) was discovered in 1914 with the field growing substantially from the 1980's onward, given the wide range of possible IL's, their non-volatile nature and their capability as a solvent without being a component of the reaction [18]. Also they have a high electrochemical and heat stability as well as high ionic conductivity, leading to the hypothesis that ionic liquids may increase charge mobility and the stability of perovskites. A review about the subject was made by Subrata Ghosh and Trilok Singh[19], citing many positive effects. These include the reduction of pinholes (optimum IL concentration was 1wt%) due to retarded crystallization, reduced surface roughness, good passivation layer between the perovskite and electron transport layer, enhancement in light absorption, increased stability under inert atmosphere due to the hydrophobic nature of some IL's. In case of the ionic liquid 1-ethylpyridinium chloride, the surplus of electrons from the pyridine rings neutralize trap states present at surface and grain boundaries. It must be said that for every study found, lead was used as cation. In this paper, 3 different IL's with the short hands EMIMBF4, EMIMBT and EMIMOTF (full chemical names are in the methodology section) are used as the additives and surface passivation agents in the 2D/3D tin films. We investigated the effect of the ionic liquid on the morphology, crystallinity, absorption and photoluminence of the tin perovskite films. Finally, we reveal the effect of the ionic liquid on the performance of the 2D/3D based tin solar cells.



(a)

Figure 1: *Structure of a perovskite crystal with general formula* $ABX_3$*[20].*

## 3 Theory

In this section most of the important phenomena regarding the study of perovskites will be discussed.

### 3.1 Perovskite crystals

Although not often seen in daily life, perovskite crystals can be found in the earth's crust and are lately in the interest of many researchers due to the remarkable properties. As displayed in the first figure, a pure crystal consists of 3 molecules and one may ask which mix of compounds will form this structure. Victor Moritz Goldschmidt was a famous mineralogist[21] and came up with a tolerance factor regarding size of the molecules. It is stated as:

$$t = \frac{R_a + R_x}{\sqrt{2}(R_b + R_x)} \tag{1}$$

with $R_a$ the radius of the A-cation, $R_b$ the B-cation radius and $R_o$ the radius for the X-cation[4]. A value of t from 0.8 to 1 makes for cubic 3D perovskites. It is suspected that the change in structure influences the interaction with light and a cubic structure is preferred. Above a certain temperature the crystal will decompose. For silicon this temperature is around 450 $C^o$ while for tin perovskites it is more around 150 $C^o$, meaning less energy is required to fabricate perovskite cells. The formation of perovskites is a self induces process and most additives will hinder this formation. Within the experiment the perovskite is actually formed by removing the solvent for the constituent parts during spin coating, meaning the annealing after spin-coating in the experiment is done for removing parts of (anti-)solvents from the crystal; not to form the crystal. This leads to the topic of crystal growth, a big factor in the fabrication of solar cells. As will be discussed later, big crystals with a flat surface are desired for the solar cell. However due to the chaos of the outside world, defects are inevitable leading to a poly-crystalline structure with multiple crystals called grains, meeting at grain boundaries, like borders of countries. Thermal annealing is a technique used to minimize these boundaries, heating the crystal up to a level where old crystals can decompose and form new crystals after which the crystal is slowly cooled to minimize heat stress caused by thermal expansion. However because the specific chemical composition used is unstable at temperatures above 100$C^o$, this method is not ideal for improving morphology in our case.

### 3.2 Device structure

As discussed there are many parameters to take into account when making a solar panel and optimizing one may lead to a less optimized value for another parameter. There is a very delicate balance for the structure regarding an completely optimized device for converting sunlight into electrical energy. To name an example, one might want to make the perovskite layer as thick as possible since then it has more chance of absorbing light. However if the thickness is larger than twice the average diffusion length, most carriers will not reach the transport layer and the efficiency will go down. Likewise there is the desire for big grains as they reduce trap states at grain boundaries, lead to greater stability and show good optoelectronic properties. Bigger grains lead however to a rougher surface of the film and pinholes between grains. The former is bad since it increases the surface at the interface and therefore increases trap states, the latter is bad as it leads to voltage drain and eventually a short circuit of the device. We will go over every layer to constructively explain why certain materials and thicknesses were chosen:

**ITO layer:**
Indium Tin Oxide (ITO) is a conductive material that is also transparent and flexible, making it an ideal contender for the upper conductive layer in a solar cell. There are not many materials having the same set of properties since metals are never transparent and most organic materials show insulating behavior. Another nice property of the material is the high reflectance of infrared light which may be harmful to the device. Other transparent conductiving oxides are $TiO_2$, $SnO_2$ and ZnO. Their work voltage also greatly influences the open circuit voltage[22]. The thickness of the ITO layer is not too significant, although it should be thick enough to block most of the infrared light and conduct electricity.

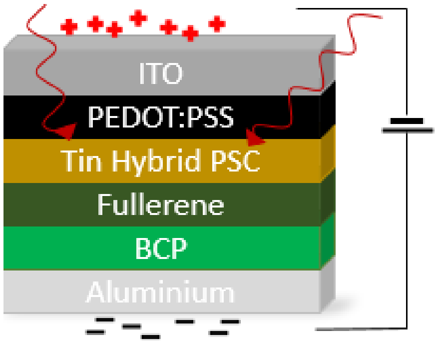
**PEDOT:PSS layer:**
This flexible transparent polymer material shows good hole mobility making it a generally used material in the field of optoelectronics and is found often in the literature. A downside of the material is the hydrophilic nature which means one must assure the material to be very dry when applying another layer. The thickness should be great enough to block most electron carriers, as to prevent recombination of electrons and holes as much as possible. For the devices this thickness is around 50 nm.

**Perovksite layer:**
The active layer. The thickness should be great enough to absorb most light but preferably not much more than twice the diffusion length of the carriers to avoid recombination; optimized around 360 nm.

**Fullerene:**
Fullerene(C60 or buckyballs) acts as the electron transport layer and is widely used for the use of n-i-p and inverted solar cell structures. The structure of a molecule somewhat resembles a football and the material is flexible. Note that from here on materials do not need to be fully transparent, but a high reflectance or transmittance is desirable since it will make light not having reacted with the active layer have a higher chance of going back through the perovskite. This layer will be 30 nm.

**BCP:**
A small layer of BCP is deposited on top of the fullerene to make the interface between fullerene and aluminum more smooth and decrease the amount of trap states/ schottky resistance at this boundary. A layer too thick can however cause recombination[23][24]. the thickness will be 6 nm.

**Aluminum:**
Aluminum is a conductive layer with high reflectance, desirable to keep the light flux through the perovskite material as high as possible. The layer thickness should not matter much.



(a)

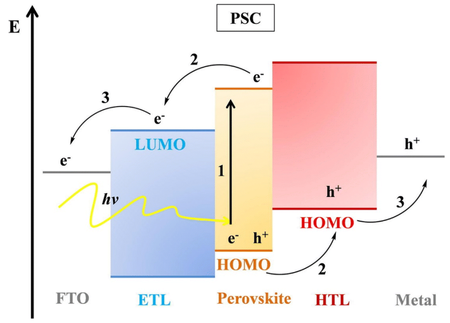
Figure 2: *A schematic of the Device structure. Incoming light is absorbed by the active layer, separating electrons and holes that will move toward the cathode and anode respectively for a n-i-p structure.*

## 3.3 Generation of charge carriers

When light is shone on a perovskite cell it will reflect, transmit or be absorbed. The last of these is where solar energy comes from. To understand it with a little more detail, there should be some clarification about the electron structure in a perovskite material. There is clear evidence for perovskites having a band structure with a band gap between the maximum valence band (MVB) and minimum conduction band (MCB); a semiconductor. electrons can only have energies equal to some band but due to lots of degenerate states above and below the band gap there are plenty of possible 'sites' for the electron to exist. The Fermi energy gives the highest occupied energy state of electrons at 0 kelvin and will lie exactly in the middle of the band gap for intrinsic semiconductors. When the temperature increases or photons bump into the electrons the electron may become excited and hop from the VB to the CB, called a hot carrier. From the photoelectric effect this can only happen when the energy of the photon is higher than $E_{gap}$, the energy difference between the MVB and MCB. This hot carrier has excess energy and will very likely fall back to the MCB. The excited electron leaves a hole at the VB. From here multiple things can happen, but for now we will focus on the desired process. The desired process in a tin perovskite is the excited electron travelling over the CB away toward an cathode through the electron transport layer (ETL), where the potential energy of an electron is low and similarly the excited hole travelling toward an anode (HTL), creating a voltage and therefore energy. The amount of extracted electrons divided by the amount of incident photons is called the External quantum efficiency (EQE).

## 3.4 Recombination

When electrons get excited a lot of different processes can take place. An unwanted effect is recombination, where the excited electron (eventually) recombines with a hole and falls back to the VB. One must realize that this process takes place all the time due to thermal excitation ($kT > E_{gap}$) and when the electron directly falls back from CB to VB it is known as radiative recombination. Another possibility is the electrons ending up in a trap state; a local state not reachable before in between the CB and VB that can trap the electron. This electron is blocked from recombining for a certain meta stable period and will eventually recombine to the VB, called irradiative recombination. These states greatly influence device performance by 'catching' the excited electrons and placing them back to the VB, converting the potential energy to heat instead of electricity. Trap states can arise from impurities, vacancies inside the crystal, grain boundaries, bad surface contact among other things.



(a)

Figure 3: *Several processes within the device. (1) light exciting an electron. (2) carriers reaching the transport layer. (3) carriers getting extracted by virtue of minimizing energy[25].*

## 3.5 Solar radiation

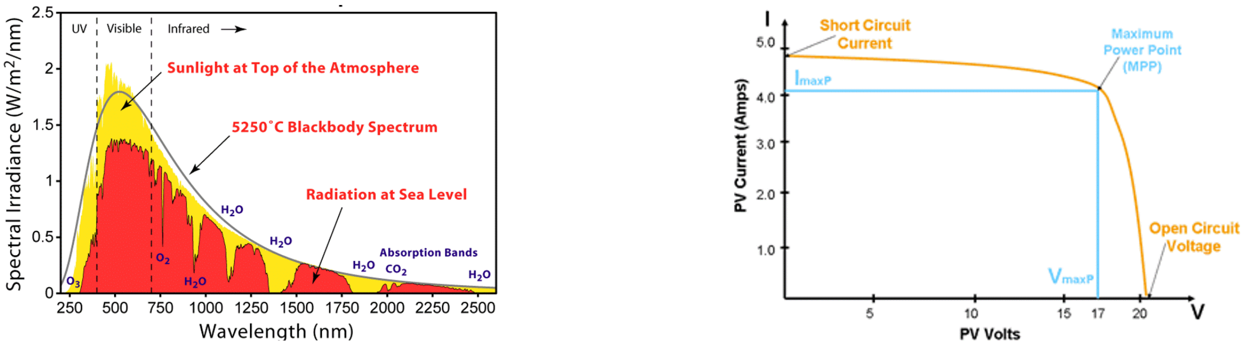
The absorbance and EQE for solar panels should be adjusted to the light spectrum of the sun. Many years ago this spectrum was theorized by the famous Max Planck. For the sun, most light is emitted in the green region, however the atmosphere also influences the spectrum by absorbing some wavelengths depending on the composition. Furthermore there is a difference in intensity for light from the sun depending on the place on earth. When building a solar panel for a satellite the intensity is different than for a tropical region and when light travels to a northern place it will pass more atmosphere than at the equator. When measuring the efficiency most researchers use the AM 1.5 intensity, meaning they use a white lamp, resembling somewhat the solar spectrum, when the light has traveled a distance through the atmosphere that is 1.5 times greater than it would when traveling toward the equator. It is equivalent to the intensity at a latitude around $48^o$[26], the latitude where most nations developing solar panels are not far away from.

## 3.6 Electronic properties

Often people talk about the efficiency of a solar cell, $\eta$. The basic parameters amounting to this efficiency will be discussed here. A general formula for $\eta$ is given as :

$$\eta = (Voc * FF * J_{sc})/I_{in} \tag{2}$$

With $\eta$ the dimensionless efficiency, $V_{oc}$ the open circuit voltage [V], $J_{sc}$ the short circuit current [A*m$^{-2}$], FF an dimensionless factor and $I_{in}$ the incoming intensity of the light [W*m$^{-2}$]. Be reminded that a (good) solar cell is a diode meaning that current will flow easily in one direction but is limited in the other direction. The $J_{sc}$ simply gives the current measured when illuminated and no voltage is applied, comparable to the EQE of the device. Then one must realize that current is not something one can store and voltage is needed for batteries. So the next step is applying a increasing voltage bias until the current is exactly canceled by the voltage. This point is called the $V_{oc}$ and there is no current present anymore. This point will however yield not any power since the current is completely blocked. The interesting point for voltage is where current is still running relatively high, while the applied voltage is also relatively high. This is where the important properties of a semiconductor come in, measured as the fill factor FF, influencing the point where I(V)*V is maximum (MPP, see figure 4). Some factors that can negatively influence these parameters are trap states, lowering the $V_{oc}$ and FF; bad contact lowering the $I_{oc}$; small grains causing less diffusion length, lowering $I_{oc}$; conductive additives increasing back ground carriers, lowering $V_{oc}$. Background carrier density can also influence the fill factor. This is caused by doping of the crystal semiconductor by increasing electron donors or acceptors and will eventually lead to a degenerate semiconductor with metallic conductance.



(a) (b)

Figure 4: *figures regarding section 2.4 and 2.5. (a) Spectrum of the sun including absorption by components from the atmosphere[27]. (b) An hypothetical I-V curve where the maximum power output is highlighted[28].*

# 4 Materials and Methods

## 4.1 Used materials

*From TCI:*
Phenyl ethyl-ammonium iodide (PEAI) >98%, Formamidium hydro iodide (FAI) >98%, Anhydrous diethyl ether >99.5%.
*From Sigma Aldrich:*
Tin iodide ($SnI_3$) 99.99%, Tin fluoride ($SnF_2$) >99%, Anhydrous dimethyl formamide (DMF) >99%, Anhydrous dimethyl sulfoxide (DMSO) >99.8%, 1-Ethyl-3-methylimidizolium trifluoromethanesulfonate (EMIMOTF, Figure 5a) >98%, 1-Ethyl-3-methylimidizolium bis(trifluoromethylsulfonyl)imide (EMIMBT, Figure 5b) >98%, 1-Ethyl-3-methylimidizolium tetrafluoroborate (EMIMBF4, Figure 5c) >97%, Anhydrous Toluene, Anhydrous chlorobenzene, Anhydrous methanol.

*Other Suppliers:*
ITO substrates, thin films, glass substrates, PEDOT:PSS.

## 4.2 Fabrication

Before device fabrication the ITO substrates were wiped multiple times with a glove and soap heated at 120 $C^o$, then put in a circulating water bad for 7 minutes and rinsed twice for at least 10 minutes by sonication in demi-water, acetone and isopropanol sequentially. After briefly blowing them with a nitrogen gun they would be put in a sample holder. Prior to fabrication the substrates were put in an oven at 140 $C^o$ for at least 3 minutes and threaded with UV-ozone radiation for 15-20 minutes to make the surface more hydrophobic. PEDOT:PSS was filtered by an $0.45\mu$ m syringe filter and deposited on the ITO surface, after which it was spin-coated at 3000 rpm, 1000 rpm/s for 60 s. After this the substrate was heated at 140 $C^o$ for at least 10 minutes and quickly transferred to the glovebox. There the solutions would be stirred and ready for deposition. The solutions containing different ratios of ionic liquids were spin-coated on the substrate at 4000 rpm, 2000 rpm/s for 60 s, dripping 0.7 ml diethyl ether or toluene at 20 s onto the substrate after spin starts(there were some small variations in these last parameters depending on the experiment). Hereafter the films were annealed at 100 $C^o$ for 20 minutes, put in the evaporator for fullerene (30nm) and BCP (6nm) were they were evaporated on the substrate respectively. Lastly an aluminum layer of 100 nm was evaporated. The now finished devices would always be in glovebox conditions. For measurements the ITO contact needed to be exposed so, using a sharp knife, the layers on top of the contact surface would be scraped of.

## 4.3 Measuring equipment

**I-V measurement:**
The first executed measurement would be the solar simulation, set up by the technicians of our faculty inside one of the glove-boxes. Always the setup would be calibrated using a highly stable silicon solar cell and cooled with liquid nitrogen to be at a temperature of 295+-1 K. Then a forward an backward sweep would take place from -0.2 to 0.8 volt with 0.01 volt increment under luminescence of one sun AM 1.5 G, giving an I-V curve for every area on the device. From this the most efficient area would be determined and dark measurements were taken on that surface. Sometimes the best efficiency would only be reached after multiple light measurements due to excited trap states being eradicated by the light. The error for this machine was small while taking multiple measurements would influence the samples.

**EQE measurement:**
This setup was in open air, requiring an air tight sample holder that would be taken out of the glovebox with the devices. An Ophir detector was used for calibration, having the calibrating device well aligned with the filters of the light. These filters would filter certain wavelength from the white light source, leaving wavefronts of (almost) pure wavelength light ranging from 400 to 1400 nm. The sample would be well aligned with the light beam and connected to a Keithley Source meter, giving a certain short circuit current for every wavelength, ending up with a spectrum of the external quantum efficiency (EQE) for certain wavelengths. This measurement is particularly useful for solar cells as it gives information about the absorbance spectrum

for hot carriers which should look alike the radiation spectrum of the sun for the most effective solar cell. Later results will show that the PSC somewhat resembles this spectrum.

**AFM measurement:**

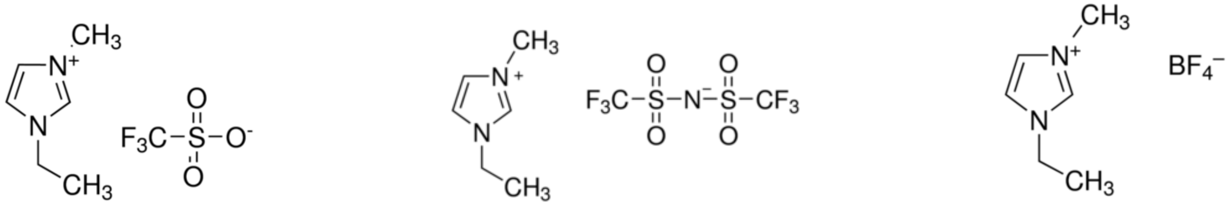
For a study of the morphology inside the PSC atomic force microscopy was used, a technique developed near the end of the 20th century, giving 3 dimensional graphs from the surface of a material. From these graphs the surface roughness and crystal grain size can be estimated, which are important factors for solar cell performance and durability. To summarize briefly, a very, very fine tip made out of silicon, attached to a cantilever, is brought just above the surface of a sample. By monitoring the reflecting beam of a laser shone on the cantilever the deflection of the tip can be determined with very high accuracy. From here multiple systems diverge; the AFM setup used here has the tip vibrating and interacting with the surface, leaving changes in frequency and amplitude of the vibrating tip. Using some hardcore feedback electronics the frequency of the ''tapping" from the tip is kept constant by changing the height of the cantilever, yielding the height of the surface at that point. Then using a piezo electric material that changes volume linearly with applied voltage, there is made a sweep over a given area. This technique can give extremely detailed images, much better than those of microscopes. The calibration of the laser onto the cantilever was done manually, as was the intensity of the reflected laser beam onto the detector. This together with the sharpness of the tip, outside vibrations and feedback settings gave the level of detail. For this measurement separate samples needed to be prepared, using a glass fully covered with ITO and PEDOT, all as discussed in the fabrication section. The films were however not coated with fullerene, BCP and aluminum, leaving the perovskite layer as the outside layer. Oxidation of the tin was discussed and claimed to have only minor impact on the morphology of the polycrystalline film which is convenient as the AFM setup is in open air. The supplier is Bruker. Later on the RMS roughness of samples is calculated; a statistical value representing deviations in the average height of a surface using a gaussian distribution[29]

**Absorbance:**

A relatively simple measurement where there is a beam of light, shifted over a spectrum of wavelengths, shone on a sample to measure the transmittance at the other end. From the transmittance the absorbance can be calculated i.e. A=-log(T), giving information about the absorbance of certain wavelengths by the sample. Within the study a 2 point measurement was conducted where there is reference sample with an ITO and PEDOT:PSS layer and without active layer, to process and cancel out the effects from those layers on the absorbance. The measured sample is the same as for AFM with ITO, PEDOT:PSS and the active perovskite layer. These samples were first measured for their absorbance, as both experiments took place in open air and the oxidation process does influence the absorbance of the perovskite layer. Higher absorbance around the solar radiation spectrum is of course desired. The supplier is Shimadzu.

**XRD measurement:**

To study the effects of ionic liquid on the perovskite crystal, a XRD measurement was conducted. Herein X-rays are radiated on the sample at a certain incident angle. A X-ray detector at that same angle but mirrored detects the intensity of the reflected beam. The beam can interfere constructively or destructively with itself depending on the lattice parameters of the crystal, called Laue diffraction. The XRD can be used to determine the presence of a certain structure, as the perovskite. Important parameters in XRD are the half width of the peaks and the position of the peaks, giving insight into the spread in orientation for the crystal structure and the lattice parameters of the crystal respectively. The instrument is a Bruker D8 advance.



(a) (b) (c)

Figure 5: *Schematic of the used ionic liquids. (a) 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate; (b) 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; (c) 1-Ethyl-3-methylimidazolium tetrafluoroborate. SOURCE: Sigma Aldrich*

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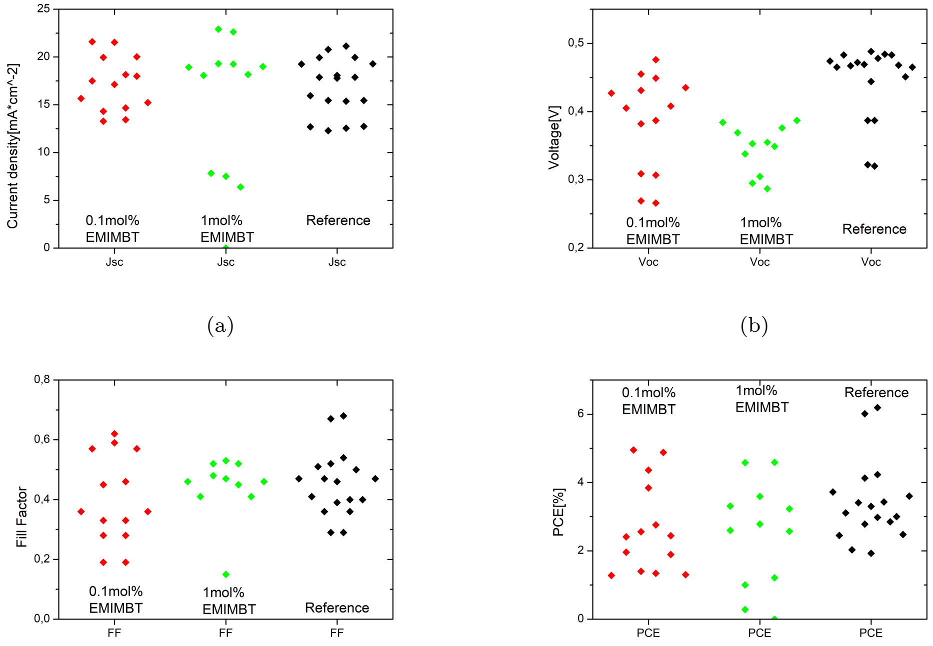
# 5 Results

Starting with the basics, there were for every week where high fluctuations in the efficiency of the reference devices, ranging from 2 to 6 percent. The origin of these differences might well be subtle differences in the fabrication and since the tin perovskites are very sensitive to conditions inside the glove box there is definitely an influence from external factors. From here there will be data mainly from good performing weeks.



(a) (b)

(c) (d)

Figure 6: *statistical box charts of the smallest area i.e. 0.04cm$^2$ for fabricated devices. (a) short circuit current. (b) open circuit voltage. (c) fill factor. (d) efficiency in PCE.*

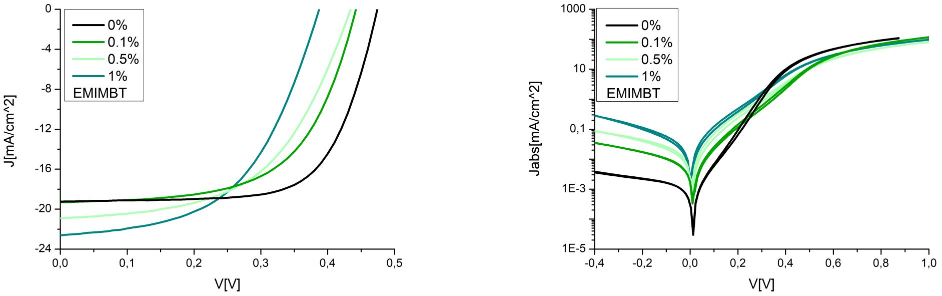
## 5.1 Device performance

Most devices, build with a large degree of impurity or within dirty glovebox conditions, showed bad stability in the brightly illuminated environment and drop in efficiency over the time taken for measurements. Other well composed perovskites showed much less of this degradation. Therefore now there is focused on the best performing devices, as they show less distorted effects. The error in the measurement is in the order of milli-volts but due to the big fluctuations in performance the precision is bad anyhow. Also one must keep in mind that for most measurements the device performance changes during the experiment, making it difficult to quantify results.

| Device | $J_{sc}$ | $V_{oc}$ | FF | PCE |
|---|---|---|---|---|
| REF | 16.94 | 0.557 | 0.66 | 6.19% |
| 0.1% | 20.93 | 0.500 | 0.59 | 6.15% |
| 1% | 19.67 | 0.413 | 0.61 | 4.97% |

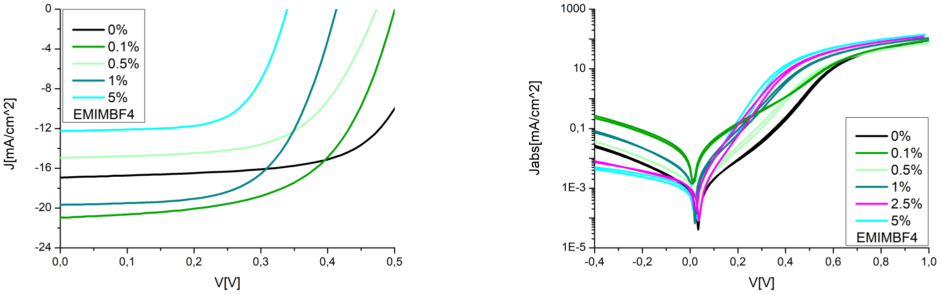
| Average | $J_{sc}$ | $V_{oc}$ | FF | PCE |
|---|---|---|---|---|
| REF | 15.19 | 0.478 | 0.41 | 2.90% |
| 0.1% | 15.34 | 0.420 | 0.36 | 2.26% |
| 1% | 13.89 | 0.380 | 0.40 | 1.73% |

Table 1: *LEFT: Important electrical properties of champion devices made without IL, 0.1mol% EMIMBF4 and 1mol% EMIMBF4. RIGHT: Average properties over all devices with the indicated amount of EMIMBT.*



(a) (b)

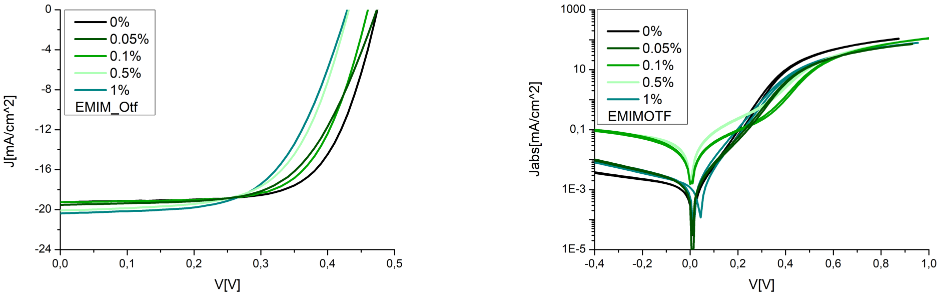
Figure 7: *I-V plots from SolarSim measurements regarding the best performing device area. (a) EMIMBT under 1.5AM light. (b) semi-log EMIMBT under dark conditions.*



(a) (b)

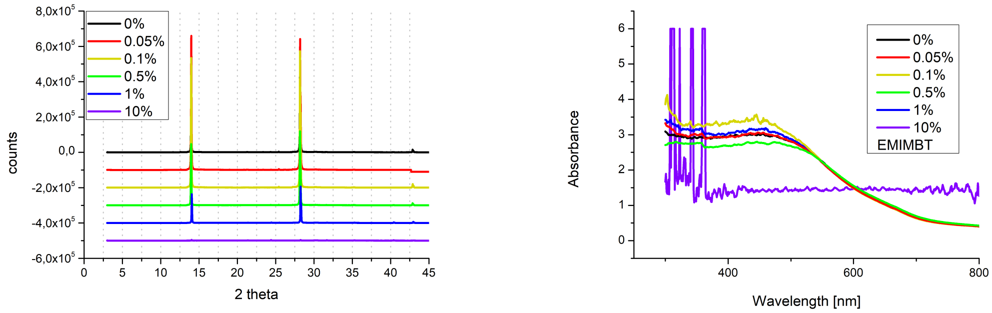
Figure 8: *I-V plots from SolarSim measurements regarding the best performing device area. Note the exceptional case of 5mol% IL. (a) EMIMBF4 under 1.5AM light. (b) semi-log EMIMBF4 under dark conditions.*

Also a photo luminescence study was conducting by a member of the group in order to look at the bandgap of the material and the lifetime of excited electrons.



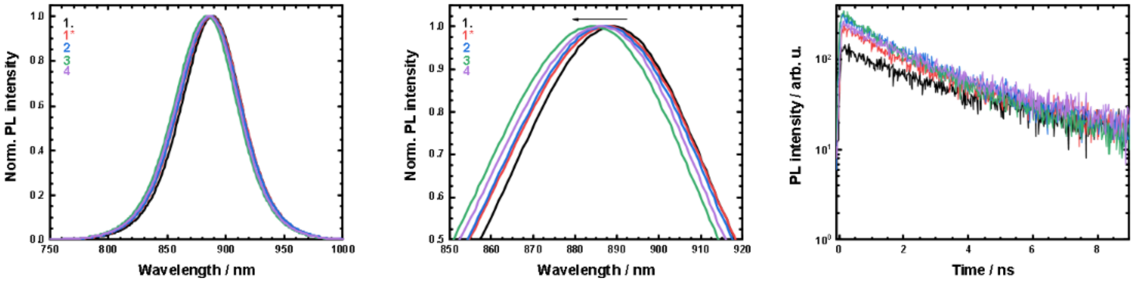
(a) (b)

Figure 9: *I-V plots from SolarSim measurements regarding the best performing device area. (a) EMIMOTF under 1.5AM light. (b) semi-log EMIMOTF under dark conditions.*



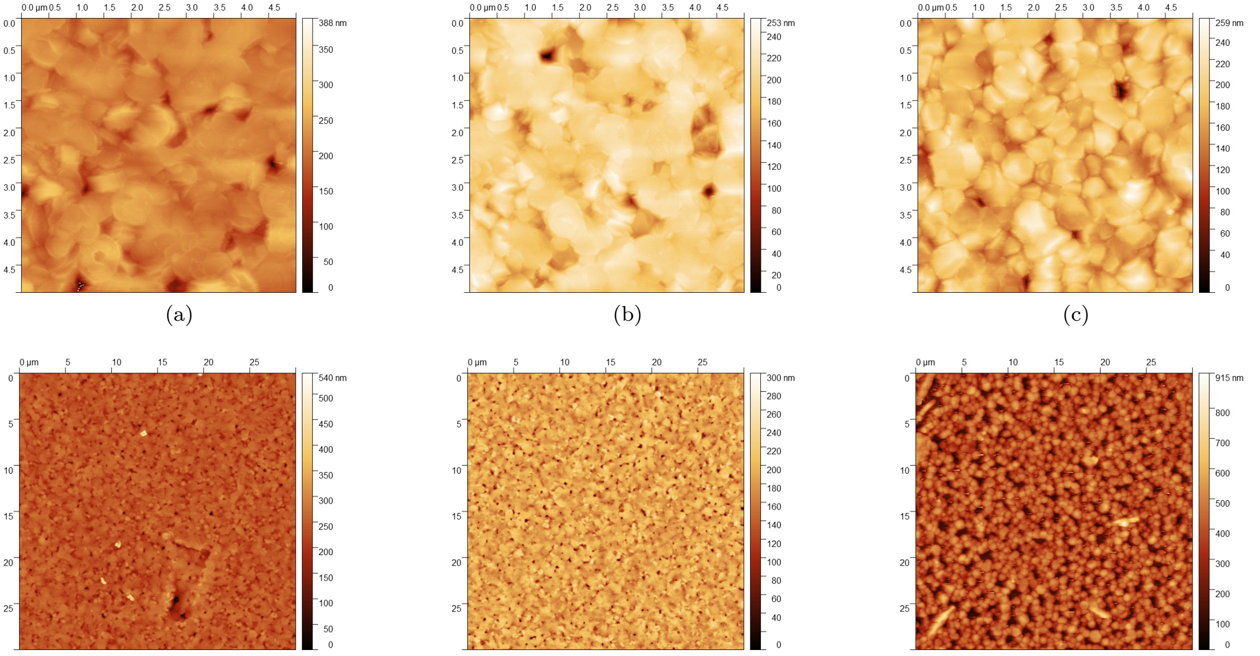
(a) (b)

Figure 10: *(a) XRD plot of counted reflected x-rays versus the incident angle multiplied by 2. there is an increment in the vertical direction for the different plots. (b) Plot of the Absorbance.*



(a)

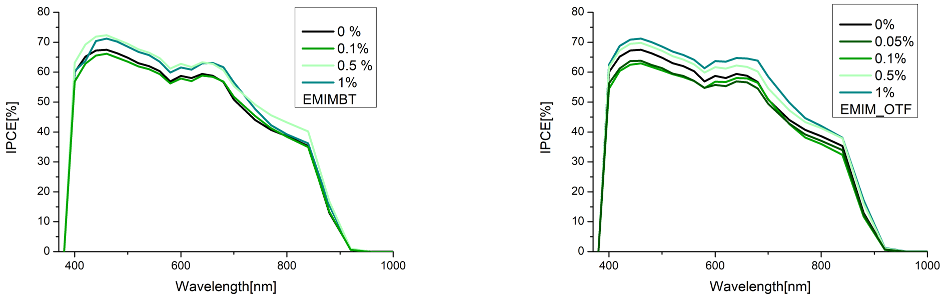
Figure 11: *Photo luminescence study regarding EMIMBT with 1-Reference; 2-0.1mol%; 3-0.5mol%; 4-1mol%. Note that the second measurement on the reference gave different results.*



(a) (b) (c)

(d) (e) (f)

Figure 12: *AFM surface plots. (a) Reference device 5 µm. (b) 0.1 mol% EMIMBT 5 µm (c) 0.5 mol% EMIMBT 5 m. (d) Reference device 30 µm (e) 0.1 mol% EMIMBT 30 µm. (f) 10 mol% EMIMBT at 30µm.*



(a) (b)

Figure 13: *The EQE measurement data showing the non-corrected yield of electrons from the photon flux at certain wavelengths. (a) is with EMIMBT samples and (b) with EMIMOTF samples.*

# 6 Discussion

From the results we can see some interesting changes for the case where ionic liquids are present. All of the notified trends will be discussed here.

## 6.1 Change in morphology

Through the pictures showing morphology one could notice several differences for devices with differing amount of IL. To start with the extreme case of 10mol%, which showed bad absorption, virtually no peaks in the XRD and diminished device performance, that big grains have formed in clusters, creating a rough surface and bad film coverage. Possibly the perovskite constituents are in some intermediate state, forming complexes with the molecules from the IL. This explains higher leakage current of the devices using IL additive, containing so many pinholes that a short circuit is inevitable. Lowering to 1% EMIMBT, the figures show clearer grain boundaries than for the reference device. Perhaps the orientation of the individual grains differs more, creating grain boundaries that are better visible with the AFM. Below 0.5%, the effect on the grains seems to be small. Also the amount of pinholes for concentrations below 0.5% seem close to the reference value. The mechanics responsible for the features are not well understood; other groups report IL to slow down crystal growth leading to a different morphology with bigger grains and similar film coverage. There is a improvement of the surface roughness for small concentrations of IL compared to the reference (see table 3), according to the Gwyddion software used for processing, using the RMS roughness as an indicator. The statistics for roughness are based on one surface of 30*30$\mu$m, meaning it does represent the bulk material but only indicates surface effects. There is a chance surface contact may improve leading to more extraction of carriers and therefore higher $J_{sc}$.

## 6.2 Crystal structure

In order to study the effects of IL on the structure some more, XRD measurements were performed. From the XRD we observed that when adding 10mol% EMIMBT the peaks of the (110) and (220) plane were minimal. Possible reasons for the decline are the IL reacting with the perovskite and the perovskite being partially solved in the IL causing amorphous structure. Other ratio's of additive were not so destructive. To analyse the data there is made a table below showing the half width and position of the peaks. Interesting is that for small ratio's of EMIMBT there is no change in the position of the peak, while for 1 mol% there does seem to be a small change. The change is however within the error margin, suggesting there is in fact no trend present. Lastly we notice that for 1 mol% the half width of both planes is more narrow than for the other cases, suggesting a better crystallinity and crystal orientation for 1mol% w.r.t reference. Also here the effects are close to the error margin.

| Device | $W_{1/2}$(110) | $W_{1/2}$(220) | $X_{pos}$(110) | $X_{pos}$(220) | RMS roughness |
|---|---|---|---|---|---|
| REF | 0.075 | 0.064 | 13.964 | 28.174% | 26.35 nm |
| 0.1% | 0.079 | 0.114 | 13.964 | 28.174% | 22.15 nm |
| 0.5% | 0.077 | 0.074 | 13.964 | 28.174% | 6.253 nm |
| 1% | 0.070 | 0.069 | 14.046 | 28.256% | 25.14 nm |

Table 2: *Results from the XRD crystal analysis made by solution without IL, with 0.1 mol% EMIMBT and 1 mol% EMIMBT. Also the roughness of the films is displayed, extracted from the AFM measurement.*

## 6.3 Increase in $J_{sc}$

There is some evidence for an increased $J_{sc}$ when ionic liquid is added, probably due to increased grain size and/or better crystillanity. After a certain molar weight however, the short circuit current seems to decrease again, likely because of the bad film coverage and 'intermediate' states caused by IL left in the active layer. The EQE measurement also showes a higher EQE, especially at higher wavelengths. Regarding the EQE it must be said that for every time the EQE was measured (5 times) samples with a specific amount of IL performed better than the reference every time, but that specific amount was different for different weeks i.e. slightly different fabrication, meaning that a 1mol% additive was sometimes better and other times a 0.1mol% performed better. The $V_{oc}$ seems to decrease for increasing amount of ionic liquid, likely due to pinholes forming more frequently with increasing IL. In the first week of measuring, an excess of ionic liquid(around 5%) was added and while it maintained the semiconductor properties both the $V_{oc}$ and $J_{sc}$ were decreased. The reason for this may be a rougher surface between the perovskite and electron transport layer or because the residue ionic liquid has an insulating effect on the charge transport. When conducting a photo luminescence test, the band gap seemed to have the slightest blue shift for adding IL although the peak position would remain from 886 for the biggest blue shift to 890 nm for the reference (corresponding to a $E_{gap}$ of 1.39 eV) and lifetime was also similar. The fragility of the samples made it hard to conduct the photoluminescence study, given that the samples showed different results when measured a second time, indicating the pulses from the machinery were altering the film. Nonetheless the difference in $J_{sc}$ did not seem to originate from a change in band gap or lifetime. Also when looking at the statistics, the increase is not apparent, meaning that reproducibility is not exactly improved with or without IL in tin perovskites and different conclusions may be formed when analysing the top devices or analysing all devices together. the deviation in results make it hard to quantify results on a large scale and because good results are likely the least polluted, distorted devices. In my opinion the champion devices tell more about device performance than a bulk where many devices are degraded up to a point where added IL is no longer the limiting factor for parameters. The similarity in statistics for the $J_{sc}$ indicates however that the EMIMBT IL did not have major impact on the short circuit current.

## 6.4 Difference between IL's

From the I-V curves one can notice that for EMIMOTF there is less spread in the results than for the other 2 ionic liquids, even when 1 mol% is added. It is a pity that this IL could not be investigated further as it showed the most promising results. During the last week of testing there was one more trial where an additive of 0.5 mol% EMIMOTF was the best performing device, be it that the batch did not show better PCE than 3 %. When a batch with EMIMBT and EMIMOTF were made together (the related I-V curves are plotted in the results) it showed better results for EMIMOTF, giving 5.89% PCE instead of 5.1-% for EMIMBT (both had a concentration of 0.1 mol%). Why does this IL cause different results than for the other 2? of the 3 IL it is the only a-symmetric molecule and the only one with oxygen bound by a single orbital to the remaining molecule. The differentiation may lie in the positioning of the liquid within the crystal, meaning it may reside at the surface or between grains and less may reside in the active layer after spincoating. Since most of the measurements were conducted on EMIMBT, it is not possible to elaborate. Also it is not possible to compare between EMIMOFT and EMIMBF4 as they were never produced in the same batch, meaning the ratio's for the solution and glove box conditions were different, inevitably leading to uncorrelated changes in result.

## 6.5 Increase in absorbance

There seems to be an slight increase of absorbance for wavelengths of 500 nm and below. Above 500 nm value the absorbance coincide for all ratio's except the 10mol% case. In this extreme case the absorbtion looks very different, absorbing light across the whole spectrum, possibly due to scattering induced by the rough surface of the active layer. As shown before, the bandgap and lattice constanst remain virtually unchanged with IL additive so the increase in absorbance must come from somewhere else. The origin of the increase may be have to do with the refraction index of ionic liquids. For some IL's there are test results showing an increase of the refractive index for higher wavelengths. Let us be reminded that light slows down in fields with a high permittivity and or permeability, meaning the refractive index is high. This will make light have a longer presence inside the material to react with particles. The ionic liquid could slow down the light[30]. A strange outcome is however the 0.5 mol% having less absorbance in the shorter wavelength regime, while both 0.1 mol% and 1 mol% show better absorbance. Another test would be needed in order to attribute this phenomenon to the presence of the IL instead of some external factor. If what is observed is really the case it excludes the proposal of IL slowing down light significantly to boost absorbance, where every higher concentration of IL should coincide with a higher absorbance.

## 6.6 Trials with Spin-coating

There has been one batch where EMIMOTF diluted with toluene was spin-coated on top of a perovskite solution, alike [17] . The perovskite solution would be fabricated with conventional methods after which it was annealed for 13 min around 95 $C^o$. Then the toluene solution with or without IL would be spin-coated on top of the formed perovskite and the sample would be annealed for 5 minutes. An solution with 10 mol% EMIMOTF solved in toluene showed better PCE than a reference where only toluene was spin-coated on top of the formed perovskite layer. However the experiment was likely faulty as there is some evidence for the perovskite layer having absorbed the IL instead of IL forming a layer on top of the perovskite crystals, due to the 2nd annealing step. Therefore an improvement would be to not anneal a second time, where the heat would make it able for IL to be absorbed, but to rest the sample for an adequate time wherein all the toluene has been evaporated from the surface, leaving a IL layer on top of the perovskite. This experiment was prepared but could not be fulfilled due to materialistic difficulties.

## 6.7 Error in the measurements

Statistical error analysis is hard to obtain when dealing with tin PSC's. This is due to a lot of external factors influencing the outcome of measurements, as well as measurements interfering with the samples causing results to be influenced by the time and intensity of measuring. Even though the precision of the measurements could be very good, accuracy is often flawed because of the sensitive nature of tin perovskites. Extremely consistent methodology and sequencing/timing are needed to obtain good results. Also in some weeks there was indication that the sequence of spin-coating was influencing device performance since the spin-coating alters the amount of solvents in the glove-box environment. To reduce this effect, the glove-box was quick-perged after 3 devices were spin-coated during the final weeks.

# 7 Conclusion

Over the course of several weeks several devices were fabricated containing different types and concentrations of ionic liquid. The incentive for this research were the reported improvements in efficiency and stability within lead perovskite films when adding ionic liquid one way or another. EMIMBT, EMIMBF4 and EMIMOTF were added to the hybrid tin perovskite solution and tested for efficiency i.e. PCE, while for EMIMBT also measurements were conducted regarding morphology, absorbance, XRD, EQE and photo luminescence. From the results it seems EMIMBT has minor impact when added in small amounts while disintegrating the films when more than 5 mol% is added. Furthermore there is an impact on the morphology, showing change in surface and different grain structure. For concentrations below 0.5% the $J_{sc}$ seems to improve, while the $V_{oc}$ decreases with increasing concentrations of EMIMBT. The addition of IL to the precursor solution has no bad effects, although positive effect are hard to quantify. It shows that by picking the right IL and fabrication technique, there could be a increase in absorbance, $J_{sc}$ and eventually PCE for tin hybrid PSC's.

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