Experimental report

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Proposal: **1-04-99** **Council:** 4/2015

Title: Impact of moisture on the morphology of hybrid organometal halide perovskite films

Research area: Materials

This proposal is a new proposal

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Samples: (CH3NH3+)[PbI3]

Instrument	Requested days	Allocated days	From	To
D22	2	2	23/10/2015	25/10/2015

Abstract:

Using hybrid organometal halide perovskites as sensitizer in hybrid solar cells has attracted very high attention in the last two years due to the very high efficiencies which have been reached within this time. One of the remaining major challenges is the moisture sensitivity of the used perovskites, which seriously limits application in solar cells since under the influence of moisture the solar cells rapidly degrade (within minutes). In the planned experiment we want to investigate the impact of moisture on the morphology of hybrid organometal halide perovskite films. These films, which are used as active layers for solar cells, will be places in a humidity chamber and will be subjected to different moistures. With in-situ grazing incidence small angle neutron scattering (GISANS) we will monitor the water uptake inside the perovskite films. From the GISANS data we can understand how water incorporated into the perovskite film affects its morphology and thereby limits the usability in solar cells. Based on this knowledge routs to stabilize perovskite films against moisture can be developed. The use of deuterated water gives the unique possibility to detect water inside the films.

Impact of moisture on the morphology of hybrid organometal halide perovskite films
(Exp-No. 1-04-99)

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Recently, hybrid organometal halide perovskites have attracted very high attention in the field of next generation solar cells due to their promising photovoltaic properties and resulting high power conversion efficiencies (PCE). These hybrid perovskites are usually of the form (MA)[PbX_3] (MA=$CH_3NH_3^+$; X=Cl^-, Br^-, or I^-), and by precisely tuning composition and thin film morphology only a few years of optimization have led to PCEs exceeding 20 % [1]. Though progress in device efficiencies has been remarkable, the lead–halide perovskites have two main drawbacks: the toxicity of the water-soluble source of lead and the instability of the material to atmospheric moisture. Therefore, a lot of research focusses on improving the moisture stability of the lead perovskite, however, the process of the water uptake itself is not deeply addressed. Due to the high sensitivity of $CH_3NH_3PbI_3$ to water, it tends to hydrolyze in the presence of moisture, leading to the degradation of the perovskite at a critical humidity of 55 %rh, which could be observed by a remarkable color change from dark brown to yellow [2]. Another investigation shows that the absorption is greatly decreased after exposure to air with a humidity of 60 %rh at 35 °C for 18 h and X-ray diffraction (XRD) measurements implied the complete degradation of $CH_3NH_3PbI_3$ [3]. Thus, on the nanoscale the perovskite crystal decomposes, however, fundamental understanding of the degradation processes on the mesoscale is still missing.

Using the grazing-incidence small angle neutron scattering (GISANS) technique and introducing D_2O vapor, we probed the kinetics of water uptake at 30 ºC and 40 °C, and followed the structure evolution of the perovskite film. The use of deuterated water gives the unique possibility to detect water inside the perovskite films. For this purpose, a custom experimental chamber was introduced to the beamline which allowed the precise control of temperature and relative humidity during the experiment.

Here, perovskite films were prepared by a common 2-step process that is known to yield highly efficient $CH_3NH_3PbI_3$ perovskite solar cells [4]. To exclude other external influences we used pre-cleaned silicon wafers as substrates and transported the samples to the beamline in a low-humidity sample environment to prevent premature degradation. Then, the degradation of these films was investigated applying the following experimental protocol: First, a long

GISANS measurement of 60 minutes was done for each film at ambient humidity prior to the start of exposure to moisture. After that, a saturated salt solution was injected into a reservoir in our custom experimental chamber with a syringe and a continuous series of shorter GISANS measurements was started for the next six hours to probe the degradation of the perovskite films in-situ. Each GISANS frame had a counting time of 10 minutes as a trade-off between good counting statistics and high time resolution.

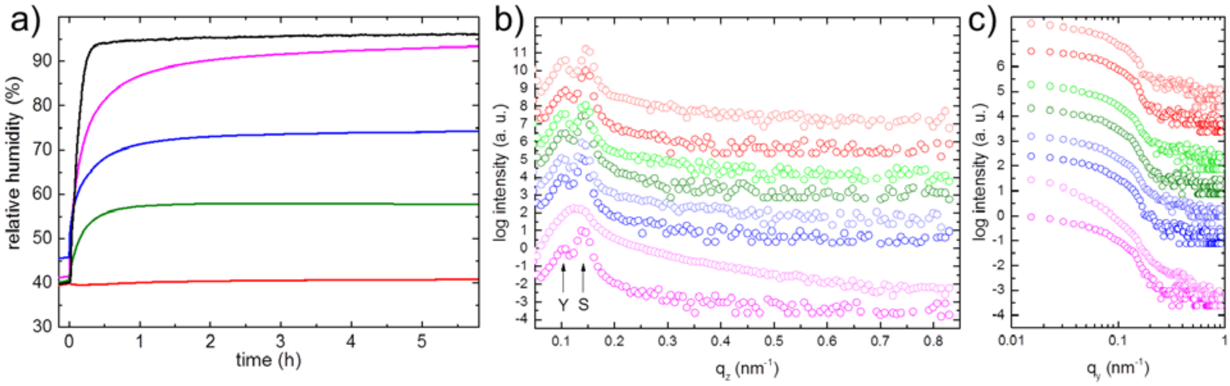

FIGURE 1: *(a) Humidities present in the experimental chamber during the in-situ GISANS degradation studies of perovskite thin films. The highest humidity was achieved at an elevated temperature of 40 °C (black line). (b) Vertical line cuts with marked Yoneda (Y) and specular peak (S) and (c) horizontal line cuts of the first and last 2D GISANS data taken at the respective humidity represented in the same color code, while the lighter color is the last image. Data are shifted for clarity along the y axis.*

The used humidities are presented in Figure 1a and are 41 %rh (red), 58 %rh (green), 73 rh (blue) and 93 %rh (pink) and thus include one humidity below the critical value of 55 %rh and one slightly above. For the green and blue curve in Figure 1b the water uptake is clearly seen from the shift of the Yoneda peak position at around 0.15 nm^{-1}, whereas no such effect is observed for the lowest humidity. For the pink curve the Yoneda peak merges with the specular peak which is a sign for the complete degradation for the film. The horizontal line cuts in Figure 1c also show the strongest change for this humidity in the low q_y-region (complete degradation) while for the others slight changes are visible at higher q_y values, indicating a shrinking of crystal domains at moderate humidities. From in-depth data analysis more details will become avaibale. Thus, from the in-situ GISANS data we can understand how water affects the morphology of perovskite thin films and thereby limits the usability in solar cells. Correlating GISANS data with in-situ XRD experiments will give a detailed explanation of water incorporation in such films. Based on this knowledge routes to stabilize perovskite films against moisture can be developed leading to higher long-term stability and less environmental hazards thus promoting fast market introduction of perovskite solar cells.

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