

## CPP 7: Perovskites - organized by Eva M. Herzig (University of Bayreuth, Bayreuth)

Time: Tuesday 9:00–16:30

Location: CPPa

CPP 7.1 Tue 9:00 CPPa

**How do solvent molecules determine the electronic structure of halide perovskite precursors?** — ●ANA M. VALENCIA<sup>1</sup>, RICHARD SCHIER<sup>1</sup>, OLEKSANDRA SHARGAIEVA<sup>2</sup>, EVA UNGER<sup>2</sup>, and CATERINA COCCHI<sup>1</sup> — <sup>1</sup>Physics Dept., Humboldt-Universität zu Berlin und IRIS Adlershof — <sup>2</sup>Helmholtz-Zentrum Berlin, HySPRINT Innovation Lab, Berlin

Hybrid metal-halide perovskites have been demonstrated as excellent candidates for opto-electronic applications such as high-performing solar cells and light-emitting devices. The quality of the resulting materials, and hence their performance, strongly depends on the solution processing conditions. For this reason, it is of paramount importance to gain insight into their initial steps of formation of the solid-state materials. To do so, we investigate the inorganic building blocks of lead-iodide perovskites in DMSO solution. In order to mimic the initial steps of the perovskite nucleation, we consider  $\text{PbI}_2(\text{DMSO})_4$ ,  $\text{Pb}_2\text{I}_4(\text{DMSO})_6$ , and  $\text{Pb}_3\text{I}_6(\text{DMSO})_8$ , as model compounds treated fully atomistically and quantum-mechanically in the framework of density-functional theory and many-body perturbation theory. Through the analysis of the computed molecular orbitals, optical spectra, and electron and hole densities we discuss and rationalize the role of electronic hybridization between solute and solvent, and the mechanisms that are responsible for the absorption and emission peaks observed in the experiments.

CPP 7.2 Tue 9:20 CPPa

**Solution-Processed Perovskite Solar Cells** — FLORIAN MATHIES<sup>1</sup>, GOPINATH PARAMASIVAM<sup>1</sup>, JANARDAN DAGAR<sup>1</sup>, and ●EVA UNGER<sup>1,2</sup> — <sup>1</sup>Helmholtz Zentrum Berlin — <sup>2</sup>Lund University, Sweden

Metal halide perovskites (MHP) are being intensively researched for solar energy conversion applications and are the best solution-processable solar cell technology to date. For scaling the technology, high throughput and material-efficient printing and coating techniques can be utilised to make larger area devices. We will here present our systematic approach translating successful processing strategies developed for spin-coating to slot-die coating and inkjet printing through in-depth rationalisation of MHP formation gained from in-situ optical monitoring. Depending on the composition of MHP precursors and solvents as well as process conditions and process quenching by e.g. an antisolvent, thin film formation proceeds via crystalline intermediate phases or directly into the perovskite phase. Optimisation of MHP precursors composition and processing conditions enabled us to recently achieve 22% power conversion efficiency in small area devices by spin-coating and 15% on large area mini-modules that are being further optimised in the near future. We are currently working on translating process conditions to obtain high quality perovskite thin films to scalable solution based deposition methods such as slot-die coating and inkjet printing. To date, we have demonstrated slot-die coating and inkjet printed small area devices with power conversion efficiencies > 15%.

CPP 7.3 Tue 9:40 CPPa

**In situ reflectometry and air flow control enables modeling of the drying process in blade coated hybrid perovskite solution films.** — ●SIMON TERNES<sup>1,2,3</sup>, TOBIAS BÖRNHORST<sup>3</sup>, JONAS A. SCHWENZER<sup>1</sup>, IHTEAZ M. HOSSAIN<sup>1,2</sup>, ULI LEMMER<sup>1</sup>, PHILIP SCHARFER<sup>2,3</sup>, WILHELM SCHABEL<sup>3</sup>, BRYCE S. RICHARDS<sup>1,2</sup>, and ULRICH W. PAETZOLD<sup>1,2</sup> — <sup>1</sup>Light Technology Institute, Karlsruhe, Germany — <sup>2</sup>Institute of Microstructure Technology, Eggenstein-Leopoldshafen, Germany — <sup>3</sup>Institute of Thermal Process Engineering, Karlsruhe, Germany

In recent years, hybrid perovskite solar cells (PSCs) have been introduced to the field of thin-film photovoltaics, exhibiting not only a steep increase in power conversion efficiencies from 3.8% in 2009 to above 25% to date, but also opening the perspective toward low-cost, large-scale solution processing. However, in order to design industrial-scale printing machines for PSCs in an efficient manner, general modeling of the dynamic drying and crystallization processes in perovskite solution films is required. This modeling must extend beyond trail-and-error optimization and beyond the commonly used, non-scalable spin coating technique. In the work presented here, we demonstrate simultaneous exact drying control by a laminar air flow and in situ film thickness measurements by reflectometry on blade coated perovskite solution

films. In this way, we derive a general model of the drying process in these solution films and correlate it with the evolving morphology, providing a strategy of optimal process transfer from spin coating to any industrial coating and drying technique.

CPP 7.4 Tue 10:00 CPPa

**Understanding the crystallization of solution processed, alloyed perovskites by multimodal characterization** — ●SHAMBHAVI PRATAP<sup>1,2</sup>, NOBUMICHI TAMURA<sup>2</sup>, ZHENGHAO YUAN<sup>3</sup>, ALASTAIR MACDOWELL<sup>2</sup>, NICOLA BARCHI<sup>4</sup>, JONATHAN SLACK<sup>2</sup>, CAROLIN SUTTER-FELLA<sup>4</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>Lehrstuhl für Funktionelle Materialien, TU München, 85748 Garching, Germany — <sup>2</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, 94720 Berkeley, USA — <sup>3</sup>Eberly College of Science, The Pennsylvania State University, State College, 16801, USA — <sup>4</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, 94720 Berkeley, USA

The crystallization behavior of solution processed hybrid plumbahalide perovskites is an ideal study to understand the formation of chemical alloys. Precursors corresponding to two different perovskites are mixed to serve as the precursor for an alloyed species. During crystallization, distinct crystalline species are isolated and characterized, as the equilibrium between the complex precursor intermediates and perovskites is transformed to the crystalline product by annealing the structure. The evolution of chemical structures is temporally resolved and the transient structures are studied for their optoelectronic transformation by photoluminescence.

40 min. meet the speakers - break

Invited Talk

CPP 7.5 Tue 11:00 CPPa

**Ultrafast spectroscopy of charge and structural dynamics in hybrid perovskites** — ●FELIX DESCHLER — TU Munich

Metal-halide perovskites have emerged as promising semiconductors for optoelectronics, in which the soft-crystalline material structure leads to unexpected excitation dynamics, and for which the underlying physics remain unexplored. Unusually strong spin-orbit coupling was predicted to introduce Rashba-type state splitting in the electronic band structure of these materials, which is expected to affect recombination dynamics and spin-populations. It remains an open question, how dynamic changes in the material structure and electronic state populations control application-relevant electronic state nature and relaxation.

In my talk I will present how we use advanced optical spectroscopy to study the dynamics of optically-excited electronic state populations and crystal structure in functional hybrid perovskite semiconductors on ultrafast timescales. I will present results on mixed-cation mixed-halide bulk metal-halide perovskites, for which I will discuss how photodoping controls the properties and recombination of electronic states, and how these can enable highly-efficient optoelectronic devices and novel functionality. I will further discuss recent results on tracking the polaronic nature of excitation on ultrafast time-scales with ultrafast time-resolved diffraction experiments, from which we extract charge localization dynamics in real time.

CPP 7.6 Tue 11:40 CPPa

**Investigating MAPbI<sub>3</sub> Thin Film Formation during Spin Coating by Simultaneous in Situ Absorption and Photoluminescence Spectroscopy** — MIHIRSINH CHAUHAN<sup>1,2</sup>, YU ZHON<sup>1</sup>, KONSTANTIN SCHÖTZL<sup>1</sup>, BRIJESH TRIPATHI<sup>2</sup>, ANNA KÖHLER<sup>1</sup>, SVEN HUETTNER<sup>1</sup>, and ●FABIAN PANZER<sup>1</sup> — <sup>1</sup>University of Bayreuth, Bayreuth, Germany — <sup>2</sup>Pandit Deendayal Petroleum University, Gandhinagar, India

Until today, the two-step processing method represents an attractive route for the thin film formation of halide perovskites. However, a fundamental understanding about the film formation dynamics in case of spin coating methylammonium iodide (MAI) on  $\text{PbI}_2$  has not been established yet. Here we apply in-situ optical spectroscopy during the two-step film formation of the model halide perovskite  $\text{MAPbI}_3$  via spin coating. We identify and analyze in detail the optical features that occur in photoluminescence and corresponding absorption spectra during processing. We find that the film formation takes place in

five consecutive steps, including the formation of a MAPbI<sub>3</sub> capping layer via an interface crystallization and the occurrence of an intense dissolution-recrystallization process. Consideration of confinement and self-absorption effects in the PL spectra, together with consideration of the corresponding absorption spectra allows to quantify the growth rate of the initial interface crystallization to be 13 nm/s for our processing conditions. We find the main dissolution recrystallization process to happen with a rate of 445 nm/s, emphasizing its importance to the overall processing.

CPP 7.7 Tue 12:00 CPPa

**Structural, optical and dielectric properties of Cs<sub>2</sub>AgBiBr<sub>6</sub>, a lead-free perovskite for photovoltaic applications** — ●MELINA ARMER<sup>1</sup>, MAXIMILIAN SIRT<sup>2</sup>, PATRICK DÖRFLINGER<sup>1</sup>, JULIAN HÖCKER<sup>1</sup>, THOMAS BEIN<sup>2</sup>, and VLADIMIR DYAKONOV<sup>1</sup> — <sup>1</sup>Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — <sup>2</sup>Ludwigs Maximilian University München, 81377 München

As conventional perovskite solar cells contain lead and therefore suffer toxicity and stability issues, finding alternative and stable lead-free materials for the application in perovskite photovoltaics has become an essential problem to be solved. In this work, lead-free Cs<sub>2</sub>AgBiBr<sub>6</sub> single crystals have been synthesized using different solution based approaches, permitting a detailed characterization of the optical and structural properties of this material. The morphology and quality of the as grown crystals has been evaluated using scanning electron microscopy (SEM), energy dispersive X-ray microscopy (EDX) and X-ray diffraction (XRD). The crystals have been characterized using steady-state and time-resolved photoluminescence (PL) spectroscopy. We observed PL in the visible region characterized by large PL lifetimes. Furthermore, the dielectric constant of Cs<sub>2</sub>AgBiBr<sub>6</sub> crystals has been measured at 9 GHz by time resolved microwave conductivity (TRMC). Using the obtained value of the dielectric constant the mobility of Cs<sub>2</sub>AgBiBr<sub>6</sub> thin films could be estimated using TRMC.

CPP 7.8 Tue 12:20 CPPa

**The Efficiency Potential of Neat Perovskite Films** — ●MARTIN STOLTERFOHT — Uni Potsdam

Perovskite photovoltaic (PV) cells have demonstrated power conversion efficiencies (PCE) that are close to those of monocrystalline silicon (m-Si) cells, however, in contrast to silicon PV, perovskites are not limited by Auger recombination. Nevertheless, compared to GaAs and m-Si devices, perovskite cells stand out by their significantly lower fill factors (FFs) which is due to a combination of resistive and non-radiative recombination losses. This necessitates a deeper understanding of the underlying loss mechanism and in particular the ideality factor of the cell. Here, by measuring the intensity (I) dependence of the external (V<sub>OC</sub>) and internal voltage (i.e. the quasi-Fermi level splitting, QFLS), we can quantify the transport resistance-free efficiency of the complete cell as well as the efficiency potential of any neat perovskite films with and without attached transport layers (TLs). Moreover, QFLS(I) measurements on different perovskite compositions allow to disentangle the impact of the interfaces and the perovskite surface on the non-radiative FF and V<sub>OC</sub> loss. We find that potassium passivated quadruple cation perovskite films stand out by their exceptionally high implied PCEs of above 28% which could be readily achieved if charge collection losses and energy alignment issues are overcome. Finally, strategies are presented to reduce both the ideality factor and transport losses to push the FF to the thermodynamic limits.

80 min. meet the speakers - break

Invited Talk

CPP 7.9 Tue 14:00 CPPa

**Structural dynamics of halide perovskites via in-situ electron microscopy** — ●CHEN LI — Electron microscopy for Materials research (EMAT), University of Antwerp, Antwerp, Belgium

In-situ heating in electron microscopy is a powerful means of investigating phase changes in materials [1], and the focused electron probe in scanning transmission electron microscope (STEM) can also be used to stimulate the movement of atoms [2]. Here we apply such dynamic STEM to directly observe ion migration in both organic and inorganic halide perovskites. For instance, a phase transition from an orthorhombic  $\delta$ -phase to a cubic  $\alpha$ -phase in inorganic CsPbI<sub>3</sub> perovskites has been tracked in atomic scale.

[1] C. Li, et. al., Secondary-phase-assisted grain boundary migration

in CuInSe<sub>2</sub>. Phys. Rev. Lett. 2020, 124, 095702

[2] C. Li, et. al., Column-by-column observation of dislocation motion in CdTe: dynamic scanning transmission electron microscopy, Appl. Phys. Lett. 2016, 109, 143107

CPP 7.10 Tue 14:40 CPPa

**The tetragonal to orthorhombic crystal phase transition in MAPI studied by time-resolved photoluminescence microscopy** — ●ALEXANDER BIEWALD<sup>1</sup>, NADJA GIESBRECHT<sup>1</sup>, RICHARD CIESIELSKI<sup>1</sup>, THOMAS BEIN<sup>1</sup>, PABLO DOCAMPO<sup>2</sup>, and ACHIM HARTSCHUH<sup>1</sup> — <sup>1</sup>LMU München, Butenandtstr. 11, 81377 Munich, GER — <sup>2</sup>Newcastle University, Newcastle upon Tyne, UK

Perovskite-based thin-film solar cells today reach power conversion efficiencies of more than 22% [1]. Methylammonium lead iodide (MAPI) is prototypical for this material class of hybrid halide perovskite semiconductors and at the focal point of interest for a growing community in research and engineering. We investigated the diffusion properties for the orthorhombic and tetragonal phase using time-resolved photoluminescence (PL) microscopy before [2]. Now we focus on the PL dynamics at the phase transition. First, the phase transition is observed in temperature dependent PL spectra, which show the correlated decrease and rise of two spectrally distinct bands. This indicates the coexistence of both phases in a limited temperature range. Second, at the phase transition, which is found to vary between grains, diffusive transport suddenly stops and only reappears upon further cooling or heating, respectively. Our spatio-temporal studies provide detailed microscopic insights into the phase transition and its influence on the carrier dynamics in large crystal MAPI thin films.

[1] M.A.Green et al.,Prog.Photovolt:Res.Appl.,26,427-436,2018

[2] A. Biewald et al.,ACS Appl.Mat.&Interfaces,11,20838-20844,2019

CPP 7.11 Tue 15:00 CPPa

**Characterization of Perovskite Precursor Solutions in order to achieve High-Performance Solar Cells** — ●MARION FLATKEN<sup>1</sup>, NGA PHUNG<sup>1</sup>, ROBERT WENDT<sup>1</sup>, ARMIN HOELL<sup>1</sup>, and ANTONIO ABATE<sup>1,2</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) — <sup>2</sup>Department of Chemical, Materials and Production Engineering, University of Naples Federico II

Despite the current success of Perovskite Solar Cells, there are still open questions how to explain intrinsic parameters in terms of stability and general photovoltaic performance of varying perovskite compositions. Deeper knowledge in coordination chemistry of the perovskite itself is one key parameter to improve and control crystallization in the solution based fabrication. Using small angle scattering we can prove, that the coordination starts in the perovskite precursor solution and differs according to the perovskite composition. The observed colloidal structures are characterized via small angle neutron scattering (SANS) and is further compared to synchrotron based small angle x-ray scattering (SAXS). Based on nuclear magnetic resonance spectroscopy the chemical composition of the complexes can be revealed, which leads us to a possible starting mechanism for nucleation and growth in perovskite precursor solutions. In our work we compare the precursor solutions of MAPbI<sub>3</sub> and MAPbI<sub>3</sub> x SrI<sub>2</sub> to a cesium containing triple cation perovskite solution, which is known to be a highly efficient and stable perovskite. Observed differences and similarities might give one reason for the divergence in photovoltaic properties of the respective full device solar cells.

CPP 7.12 Tue 15:20 CPPa

**Thermal decomposition dynamics of lead halide perovskite thin films** — THOMAS BURWIG, KARL HEINZE, ROLAND SCHEER, and ●PAUL PISTOR — MLU Martin-Luther-Universität Halle-Wittenberg

Despite the remarkable progress of lead halide perovskites, their low stability severely limits practical applications. To understand degradation pathways and pinpoint optimal compositions in terms of stability is therefore of utmost importance. Here we investigate the thermal stability of lead halide perovskite thin films grown by co-evaporation and analyze their thermal decomposition at elevated temperatures. Our approach allows to investigate the thermal decomposition by time-resolved in situ X-ray diffraction inside the vacuum growth chamber, without exposing the perovskite thin film to moisture or ambient air at any time. By applying fixed temperature ramps of 3-4 K/min. , we compare the onset of decomposition for a variety of different ABX<sub>3</sub> compositions and explore perovskites throughout the compositional space with A=MA,FA,Cs; B=Pb,Sn,(Ag,Bi) and X=I,Br,Cl. We find an increasing decomposition temperature for the series MAPbCl<sub>3</sub> - MAPbI<sub>3</sub> - MAPbBr<sub>3</sub>, where the perovskite decomposes via degassing

of MAX. The cation variation shows increased stability for CsPbBr<sub>3</sub> over FAPbBr<sub>3</sub> and MAPbBr<sub>3</sub>, mainly due to the increased sublimation temperature of CsX, which is even higher than that of PbX<sub>2</sub>. Finally, for the case of the most common and less stable MAPbX<sub>3</sub> perovskites, a series of time-resolved degradation experiments at constant temper-

atures provides detailed insights into the degradation kinetics of these materials.

**50 min. meet the speakers - break**