

CPP 57: Hybrid Perovskite and Photovoltaics I (joint session CPP/HL)

Time: Wednesday 9:30–12:45

Location: ZEU 260

CPP 57.1 Wed 9:30 ZEU 260

Growth of High-quality (FAPbI₃)_{0.9}(MAPbBr₃)_{0.1} Perovskite Single Crystals and their Optoelectronic Properties — ●JULIAN HÖCKER¹, MATHIAS FISCHER¹, MEHMET ÖZCAN², BENEDIKT BICHLER², SEBASTIAN HAMMER¹, MELINA ARMER¹, VOLKER DRACH¹, BERT NICKEL², and VLADIMIR DYAKONOV¹ — ¹Experimental Physics VI, JMU, 97074 Würzburg — ²Soft Condensed Matter Group, LMU, 80539 München

Organo lead trihalide perovskites are potentially highly interesting class of semiconductors. Particularly the perovskite (FAPbI₃)_{0.9}(MAPbBr₃)_{0.1} is one of the most important representatives of this material class. In order to further develop this complex perovskite system and thus foster its use, it is essential to investigate the chemical and physical properties of high-quality single crystals with the same stoichiometry. However, the liquid growth of perovskite crystals without seed crystals is usually challenging and becomes even more challenging with mixed cations/halides crystals, making it difficult to assess their properties. For this purpose, we have developed a new efficient re-fill crystallization method (RFCM) based on the Inverse Temperature Crystallization (ITC), which avoids seed crystals. We applied qualitative and quantitative analyses to identify the elemental composition and the exact stoichiometry of the grown crystals and studied their crystallographic properties, demonstrating a high single crystal quality. Optical and electrical measurements completed the structural and elemental analysis, and enabled us to derive relevant properties of this perovskite material.

CPP 57.2 Wed 9:45 ZEU 260

Revealing the Impact of Cesium/Rubidium Incorporation on the Photophysics of Multiple-Cation Lead Halide Perovskites — YAJUN GAO, KAI WANG, MINGCONG WANG, JAFAR KHAN, AHMED BALAWI, STEFAAN DE WOLF, and ●FRÉDÉRIC LAQUAI — King Abdullah University of Science and Technology (KAUST), KAUST Solar Center, Thuwal, Saudi Arabia

The incorporation of cesium (Cs) and rubidium (Rb) ions in multiple-cation mixed lead halide perovskites increases their photovoltaic performance. Here, the reasons for the performance increase are investigated by steady-state and transient spectroscopy techniques. The band edge absorption shows that the Cs/Rb-ion incorporation increases the band gap, while exciton binding energies remain low, in the range of a few milli-electronvolts. Low Urbach energies determined by photothermal deflection spectroscopy suggest optimized microstructures upon Cs/Rb incorporation. The charge carrier recombination dynamics indicate that Cs/Rb-incorporation reduces not only the first-order (trap-assisted) recombination, but also the second-order recombination. Upon photoexcitation, carrier density-induced broadening of the photo-bleaching following the Burstein-Moss model is observed and effective carrier masses are determined to be in the range of a few tenths of the electron rest mass, explaining the excellent charge carrier mobilities of these perovskite films. Sub-picosecond hot carrier cooling is observed, indicating a strong charge-phonon coupling. Our results reveal the impact of cesium/rubidium incorporation on the photophysics of multiple-anion lead halide perovskites.

CPP 57.3 Wed 10:00 ZEU 260

Unraveling origin of performance instability in mixed perovskite solar cells — ●MALGORZATA KOT¹, CHITTARANJAN DAS², TIM HELLMANN², CAROLIN WITTICH², IWAN ZIMMERMANN³, MOHAMMAD KHAJA NAZEERUDDIN³, WOLFRAM JAEGERMANN², and JAN INGO FLEGE¹ — ¹BTU Cottbus-Senftenberg, Germany — ²TU Darmstadt, Germany — ³EPFL Lausanne, Switzerland

A degradation mechanism of mixed perovskite solar cells is mostly attributed to the segregation of halide phases in the perovskite film. However, our studies have revealed, that the mixed perovskites degrade due to the migration of iodine and methylammonium ions across the solar cell. Nonetheless, an ultrathin RT-ALD-Al₂O₃ layer deposited on top of perovskite can very effectively limit this migration thanks to the reactive property of this interface.[1-3] Namely, there is a closed cycle of the charge transfer between ALD and perovskite films. Such ALD film doesn't cause any drastic changes in the perovskite morphology, chemical composition, optoelectronic properties or crystallinity. What more, it helps to preserve the initial properties of the film during expo-

sure to the light and ambient air under real operating conditions and thus improves the stability of the solar cells. This ultra-thin Al₂O₃ layer prepared in an unusual RT process for ALD method significantly increases the lifetime of perovskite solar cells at a very low cost bringing thus the introduction of the perovskite solar cells into mass production. [1] M. Kot et al., ChemSusChem 11 (2018) 3640. [2] M. Kot et al., Energy Technol. 7 (2019) 1900975. [3] D. Schmeißer et al., J. Phys. Chem. C 123 (2019) 23352.

CPP 57.4 Wed 10:15 ZEU 260

Phase transitions of hybrid and inorganic perovskites simulated by machine-learning force fields — RYOSUKE JINNOUCHI^{1,2}, JONATHAN LAHNSTEINER¹, FERENC KARSAI³, GEORG KRESSE¹, and ●MENNO BOKDAM¹ — ¹University of Vienna, Vienna, Austria — ²Toyota Central R&D Labs, Aichi, Japan — ³VASP Software GmbH, Vienna, Austria

Finite-temperature simulations of complex dynamic solids are a formidable challenge for first-principles methods. Long simulation times and large length scales under isothermal-isobaric (NPT) conditions are required, demanding years of compute time. We applied the recently developed on-the-fly Machine-Learning Force Field (MLFF) scheme[1] to generate force fields for several hybrid and inorganic perovskites (APbX₃, A={MA,Cs},X={I,Br,Cl}). The MLFFs open up the required time and length scales, while retaining the distinctive chemical precision of first principles methods. We study the entropy driven phase transitions of hybrid perovskites, which have never been accurately described in simulations. Simulations using machine learned potentials give direct insight into the underlying microscopic mechanisms. The ordering of the Methylammonium (MA) molecules as function of temperature is obtained. Furthermore, we relate the phase transition temperatures of different perovskites to the radii of the involved species, and we determine the order of the transitions in Landau theory.

[1] R. Jinnouchi et al., Phys. Rev. Lett. 122, 225701 (2019)

CPP 57.5 Wed 10:30 ZEU 260

The tetragonal to orthorhombic crystal phase transition in MAPI studied by time-resolved photoluminescence microscopy — ●ALEXANDER BIEWALD¹, NADJA GIESBRECHT¹, RICHARD CIESIELSKI¹, THOMAS BEIN¹, PABLO DOCAMPO², and ACHIM HARTSCHUH¹ — ¹LMU München, Butenandtstr. 11, 81377 Munich, GER — ²Newcastle 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 57.6 Wed 10:45 ZEU 260

Structural, optical and dielectric properties of Cs₂AgBiBr₆, a lead-free perovskite for photovoltaic applications — ●MELINA ARMER¹, MAXIMILIAN SIRT², PATRICK DÖRFLINGER¹, JULIAN HÖCKER¹, THOMAS BEIN², and VLADIMIR DYAKONOV¹ — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — ²Ludwigs 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 $\text{Cs}_2\text{AgBiBr}_6$ 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 $\text{Cs}_2\text{AgBiBr}_6$ crystals has been measured at 9 GHz by time resolved microwave conductivity (TRMC). Using the obtained value of the dielectric constant the mobility of $\text{Cs}_2\text{AgBiBr}_6$ thin films could be estimated using TRMC.

CPP 57.7 Wed 11:00 ZEU 260

Characterization of Perovskite Precursor Solutions in order to achieve High-Performance Solar Cells — ●MARION FLATKEN¹, NGA PHUNG¹, ROBERT WENDT¹, ARMIN HOELL¹, and ANTONIO ABATE^{1,2} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) — ²Department 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_3 and $\text{MAPbI}_3 \times \text{SrI}_2$ 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.

15 min. break

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Solution-Processed Perovskite Solar Cells — FLORIAN MATHIES¹, GOPINATH PARAMASIVAM¹, JANARDAN DAGAR¹, and ●EVA UNGER^{1,2} — ¹Helmholtz Zentrum Berlin — ²Lund 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 57.9 Wed 11:45 ZEU 260

How do solvent molecules determine the electronic structure of halide perovskite precursors? — ●ANA M. VALENCIA¹, RICHARD SCHIER¹, OLEKSANDRA SHARGAIEVA², EVA UNGER², and CATERINA COCCHI¹ — ¹Physics Dept., Humboldt-Universität zu Berlin und IRIS Adlershof — ²Helmholtz-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 57.10 Wed 12:00 ZEU 260

Photodoping through local charge carrier accumulation in alloyed hybrid perovskites for highly efficient luminescence — ●SASCHA FELDMANN, STUART MACPHERSON, SATYAPRASAD SENANAYAK, MOJTABA ABDI-JALEBI, JASMINE RIVETT, GUANGJUN NAN, GREGORY TAINTER, TIARNAN DOHERTY, KYLE FROHNA, EMILIE RINGE, RICHARD FRIEND, HENNING SIRRINGHAUS, MICHAEL SALIBA, DAVID BELJONNE, SAMUEL STRANKS, and FELIX DESCHLER — Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom

Metal-halide perovskites have emerged as exceptional semiconductors for optoelectronic applications. Substitution of the monovalent cations has advanced luminescence yields and device efficiencies. Here, we control the cation alloying to enhance optoelectronic performance through alteration of the charge carrier dynamics in mixed-halide perovskites. In contrast to single-halide perovskites, we find high luminescence yields for photo-excited carrier densities far below solar illumination conditions. Using time-resolved spectroscopy we show that the charge-carrier recombination regime changes from second to first order within the first tens of nanoseconds after excitation. Supported by microscale-mapping of the optical bandgap, electrically-gated transport measurements and first-principles calculations, we demonstrate that spatially-varying energetic disorder in the electronic states causes local charge accumulation, creating p- and n-type photo-doped regions, which unearths a strategy for efficient light emission at low charge-injection in solar cells and LEDs.

CPP 57.11 Wed 12:15 ZEU 260

Perovskite solar cells from direct co-evaporation: Impact of hole transport materials on device performance — ●MARCEL ROSS¹, AMRAN AL-ASHOURI¹, ERICA MAGLIANO¹, MARKO JOŠT¹, and STEVE ALBRECHT^{1,2} — ¹Helmholtz-Zentrum Berlin, D-12489 — ²Technical University Berlin, D-10587

Deposition of perovskite solar cell absorbers by co-evaporation offers a variety of advantages over solution based preparation such as homogeneous coating of large substrates and conformal coverage of different textures. Nevertheless, the majority of reported publications focusses on solution-based preparation of perovskite solar cells. This is likely due to the challenging evaporation characteristic of organic precursors and the limited understanding of the perovskite co-evaporation process itself. To achieve a better process control, we implement an evaporation setup with a thermal management system. This enables the deposition of high quality Methylammonium Lead Iodide perovskite films as confirmed by XRD, PL and optical measurements. To analyse the influence of substrate properties on film formation, perovskites are deposited on different hole transport materials (HTMs) such as PTAA and self-assembling monolayer (SAM) molecules. Furthermore, the impact of the substrate temperature during deposition of the perovskite is investigated. While the substrate temperature is mainly influencing the incorporation of methylammonium iodide into the film, the p-i-n solar cell performance is strongly affected by the used HTM. Finally, a stabilized efficiency over 20% is realized with the SAM hole transport layer and a proper substrate temperature.

CPP 57.12 Wed 12:30 ZEU 260

The impact of mobile ions on the open circuit voltage decay of perovskite solar cells explained by time resolved drift-diffusion simulations. — ●MATHIAS FISCHER, DAVID KIEMASCH, KRISTOFER TVINGSTEDT, and VLADIMIR DYAKONOV — Experimental Physics VI, Julius Maximilian University of Würzburg, 97074

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The open circuit voltage decay (OCVD) is a characteristic transient response of an operating solar cell after the illumination is turned off. By analyzing such transients correctly, it is possible to obtain valuable information about charge carrier dynamics in a fully functional device. When additional charged species like mobile ions are present, extraordinary features can be observed during the OCVD. We use a self-programmed transient drift-diffusion simulator involving mobile

ions with sub-nanoseconds time resolution, to show how quantitative information about the ionic species, such as concentration and diffusion coefficient can be obtained. The simulated transients showing characteristic ionic features are in excellent agreement with experimental data from methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) devices. Further, the ionic contributions to the OCVD are clearly visualized by specially resolved carrier profiles. This approach opens up new ways to interpret transient electrical measurements on perovskite based devices.