

AKJDPG 1: PhD Focus Session: Photoluminescence of halide perovskites: What does it tell us and what not? (joint session DS/AKJDPG/HL)

Perovskite Solar Cells (PSCs) have recently emerged as a new research field due to their rapid increase in power conversion efficiency. Many research groups formerly working in other fields such as in DSSC, organic solar cells and thin film solar cells, quantum dots, single molecules have jointly created a new research field. Photoluminescence spectroscopy is a technique used rather widely in all of these fields as a simple standard method. Applying specific models and theory, photoluminescence can however be converted into an advanced characterization technique. The models and analysis tools used for this have been unique to the specific fields so far and now tend to collide when PSCs are measured and analysed.

This symposium therefore aims to give a brief overview of advanced models and analysis tools which allow a more nuanced interpretation of photoluminescence emission of perovskite solar cell materials. In a mix of introductory talks, invited expert talks and contributed talks we will explore how certain models have been used to analyse PSCs and argue why and under what conditions a certain model can or cannot be applied to perovskite solar cells.

Organizers:

- Juliane Borchert, Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom
- Klara Suchan, Lund University, Kemicentrum, Naturvetarvägen 16, 22362 Lund, Sweden
- Tobias Seewald, Department of Physics, University of Konstanz, Universitätsstr. 10, 78457 Konstanz, Germany

Time: Tuesday 9:30–13:15

Location: H32

Invited Talk AKJDPG 1.1 Tue 9:30 H32
Photoluminescence Analysis of Thin Films: What can it tell us about (Perovskite) Solar Cells? — •THOMAS UNOLD —
 Helmholtz-Zentrum Berlin für Materialien und Energie

Photoluminescence analysis has been an important analytical tool in semiconductor characterization, and depending on the experimental conditions can reveal detailed information about various optical and electronic properties such as radiative recombination, non-radiative recombination, defects, carrier trapping and the quasi-Fermi level splitting[1-4]. The technique can be applied to thin films as well as to complete solar cell devices, but may require additional analysis to consider the presence of either free surfaces or built-in electrical fields, additional recombination processes as well as partial charge extraction. In the ideal case different types of luminescence measurements yield a consistent picture of the material properties and the limitations of device performance. Different aspects of such photoluminescence analyses will be discussed with a special focus on how results obtained on (hybrid) perovskites comply with the state-of-the-art knowledge on more common inorganic semiconductor materials. [1] T. Unold, L. Gütay, in *Advanced Characterization Techniques for Thin Film Solar Cells*, Wiley VCH (2011) 151-175. doi.org/10.1002/9783527636280.ch7 [2] F. Staub et al., *Phys. Review Applied* 6 (2016) 044017 [3] C. Hages et al., *Adv. Energy Mater.* 7(2017) 1700167 [4] M. Stolterfoht et al., *Nature Energy* 3 (2018) 847.

In-situ film formation studies of metal-halide perovskite layers — •KATRIN HIRSELANDT^{1,2}, RAHIM MUNIR¹, FLORIAN MATHIES¹, ABOMA MERDASA¹, EMIL J. W. LIST-KRATOCHVIL², and EVA UNGER^{1,2} —¹Helmholtz-Zentrum Berlin für Materialien und Energie, Kekuléstraße 5, 12489 Berlin, Germany — ²Institut für Physik, Institut für Chemie & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 6, 12489 Berlin, Germany

By optimizing the perovskite fabrication process during spin-coating by introduction of complex solvent blends and quenching steps, solar cells with power conversion efficiencies above 22% have been realized on small active areas. Reproducing published fabrication procedures is not trivial as process conditions vary from place to place and adapting methodologies developed for small-area devices based on spin-coating to larger area devices even less so. Understanding the film formation during different stages of processing allows for a more rational approach to translate deposition strategies to scalable processing methods.

In this study we compared the temporal evolution of MAPbI₃ and Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃ (3CAT) covered substrates during spin-coating using a fibre-optic based photolumines-

cence and reflection spectroscopy setup. Varying the time of a crystallization-inducing anti-solvent drip, we identified a much narrower process window for MAPbI₃, compared to 3CAT corroborated with scanning electron microscope images of annealed samples. We here present insight into the difference in crystallization kinetics of these different standard formulations for perovskite processing.

Invited Talk AKJDPG 1.3 Tue 10:15 H32
Defect activity in lead halide perovskite semiconductors —
 •SILVIA MOTTI — Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, OX1 3PU, Oxford, United Kingdom

Perovskite semiconductors have recently emerged as promising materials for optoelectronic applications, with photovoltaic efficiencies that have now reached over 23%. Great research effort has been employed towards understanding how the perovskite crystalline and electronic structure relates to their remarkable defect tolerance and surprisingly long carrier lifetimes and high open circuit voltages. At the same time, the material instability often interferes with experimental observations, besides posing a major challenge for commercial application. A comprehensive investigation of defect activity in lead halide semiconductors was conducted by combining computational studies with experimental evidences from optical spectroscopy. It was possible to identify the most predominant charge-trapping point defects in MAPbBr₃ and MAPbI₃ and their role in recombination dynamics, explaining the defect tolerance in these semiconductors. Moreover, the reactivity of such defects under external stimuli could be associated with the photoinstabilities observed in these materials, allowing for the development of successful strategies to control them. This understanding opens the possibility of developing intelligent fabrication methods and further optimizing performance and stability of perovskite optoelectronic devices.

AKJDPG 1.4 Tue 10:45 H32
The impact of lead iodide on the recombination kinetics in metal halide perovskites — •ABOMA MERDASA¹, ALEXANDROS KILIGARIDIS², CAROLIN REHERMANN¹, MOJTABA ABDI-JALEBI³, JONAS STÖBER², BORIS LOUIS², MARINA GERHARD², SAMUEL D. STRANKS³, EVA L. UNGER^{1,2}, and IVAN G. SCHEBLYKIN² —¹Young Investigator Group Hybrid Materials Formation and Scaling, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany — ²Chemical Physics and NanoLund, Lund University, Lund, Sweden. — ³Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge, United Kingdom.

Metal halide perovskites are promising semiconductor materials for photovoltaic devices with solar cell efficiencies soaring over 20%, but

understanding the fundamental operational principles are lagging behind. One example is the role and influence of lead iodide (PbI₂) reportedly being both beneficial and detrimental for a device. Herein, we present a study on the impact of lead iodide on the charge-carrier recombination kinetics in methylammonium lead triiodide (MAPbI₃) thin films. We simultaneously acquire spectrally-resolved photoluminescence quantum yield and time-resolved photoluminescence lifetime at excitation wavelengths ranging from 450 nm to 780 nm during hours of light-soaking, and identify a unique radiative recombination mechanism occurring at the PbI₂/MAPbI₃ interface when charge carriers are generated in PbI₂. We thereby provide important insight into the long-debated question of whether excess PbI₂ is beneficial or detrimental for charge carrier dynamics in perovskite solar absorber materials.

15 min. break

Invited Talk AKJDPG 1.5 Tue 11:15 H32
Beyond traditional use of photoluminescence: Assessing halide perovskites quantitatively and qualitatively — ●CAROLIN SUTTER-FELLA — Lawrence Berkeley National Laboratory, Berkeley, California, US

Hybrid metal halide perovskites have recently transformed the landscape of light harvesting solar energy materials while showing promise in a range of other optoelectronic applications. These materials do not only show exceptional optoelectronic properties and apparent defect tolerance but are also easy to synthesize via solution processing. Nevertheless, there are non-radiative recombination losses which have to be characterized and ideally tied back to synthesis conditions.

In the first part of this talk I will cover our work on quantitative photoluminescence quantum yield measurements under variation of the halide as well as cation. This quantity will be related to the device relevant open circuit voltage (V_{oc}) by comparing the electrically measured Voc to the optically implied Voc. In the second part I will show how in situ photoluminescence spectroscopy can be used to monitor perovskite film and nanoparticle formation. I will reveal the onset of semiconducting properties during synthesis and the correlation to other material characteristics such as morphology and crystal phase. The work provides guidance to a fast screening of the synthetic parameter space and ultimately controlled experimental procedures that yield high device efficiencies.

AKJDPG 1.6 Tue 11:45 H32
Temperature dependent charge carrier transport in MAPI single crystal thin films — ●ALEXANDER BIEWALD¹, RICHARD CIESIELSKI¹, NADJA GIESBRECHT¹, KATHRIN HANDLOSER¹, PABLO DOCAMPO², THOMAS BEIN¹, and ACHIM HARTSCHUH¹ — ¹Department Chemie und (CeNS), LMU München, Deutschland — ²School of Electrical and Electronic Engineering, Newcastle, UK

Methylammonium lead iodide (MAPI)-based thin-film solar cells today reach power conversion efficiencies of more than 20% [1]. The material is prototypical for the large class of perovskite semiconductor materials for photovoltaic applications and is therefore at the focal point of research interest to a global community. Here, we present an all-optical study of the charge carrier diffusion properties in large-crystal MAPI thin films using photoluminescence microscopy [2]. We vary the temperature between 170 K and room temperature, thus remaining in the tetragonal crystal phase [2]. We probe the local material properties of individual crystal grains within a PMMA-coated MAPI thin film and find a steady increase of the diffusion constant towards lower temperatures. In a previous paper we found that grain boundaries in such thin films act as solid walls for diffusing charge carriers [2], which we also see at low temperatures.

- [1] M. A. Green, et al., Solar cell efficiency tables (version 52), 2018.
 [2] R. Ciesielski, et al., ACS Appl. Mat. & Interfaces. 10 (9), 7974-7981 (2018).
 [3] N.O. Yamamuro, et al., J. Phys. Chem. Solids 53 (7), 935-939

(1992).

Invited Talk AKJDPG 1.7 Tue 12:00 H32
Photophysics of Sn-based hybrid perovskites — ●MARIA ANTONIETTA LOI — Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands

Thanks to the intensive research efforts of a large scientific community over the past years, lead (Pb)-based hybrid perovskite solar cells have reached impressive (>23%) power conversion efficiency. Against the initial criticism about their instability, also large improvements in the thermal and photo stability of this kind of solar cells were obtained in the last years. Despite these outstanding accomplishments, the toxicity of lead causes concerns about the possible large-scale utilization of this new type of solar cell. Among the various alternatives to lead, Sn has been recognized to have a great potential, as the Sn-based hybrid perovskites display excellent optical and electrical properties such as high absorption coefficients, very small exciton binding energies and high charge carrier mobilities. Recently solar cells with efficiencies approaching 10% have been reported. In my presentation I will report about important features of the photophysical properties of formamidinium tin triiodide. Photoluminescence spectra are highly asymmetric at the high-energy edge. This is accompanied by the unusually large blue shift of the time-integrated photoluminescence with increasing of the excitation power. These phenomena are associated with very slow hot carrier relaxation and state-filling of band edge states. Most importantly, the hot carrier photoluminescence is evident not only upon pulsed excitation but also with continuous wave one.

AKJDPG 1.8 Tue 12:30 H32
Metastable defects in perovskite semiconductors reveal microscopic insight into non-radiative processes — ●MARINA GERHARD¹, BORIS LOUIS^{1,2}, RAFAEL CAMACHO², ABOMA MERDASA³, ALEXANDER KILIGARIDIS¹, JUN LI¹, ALEXANDER DOBROVOLSKY¹, JOHAN HOFKENS², and IVAN G. SCHEBLYKIN¹ — ¹Division of Chemical Physics and NanoLund, Lund University, Box 124, 22100 Lund, Sweden — ²KU Leuven, Molecular Imaging and Photonics, Celestijnenlaan 200f, Box 2404, 3001 Leuven, Belgium — ³Helmholtz-Zentrum für Materialien und Energie GmbH, Kekulestraße 5, 12489 Berlin, Germany

Metal halide perovskites are an interesting model system for fundamental studies of non-radiative processes due to their photoluminescence (PL) fluctuations on a timescale of milliseconds to seconds, also referred to as 'blinking'. This phenomenon is attributed to the presence of metastable defects, able to switch between a passive (not quenching) and an active (quenching) configuration. Here, we study temperature dependent blinking of methylammonium lead iodide nanocrystals using PL microscopy. Monitoring the behavior of individual defects allows us to understand their concerted contribution to macroscopic quantities, such as the temperature dependent PL quantum yield. We find that both the quenching efficiency and the switching rate of the metastable defects decrease with decreasing temperature. Based on a simple mechanistic picture, we estimate activation barriers for the switching on the order of 200-800 meV. This energy range suggests that the switching mechanism could be related to ion migration.

AKJDPG 1.9 Tue 12:45 H32
Panel Discussion (with invited speakers) — ●THOMAS UNOLD¹, SILVIA MOTTI², CAROLIN SUTTER-FELLA³, and MARIA ANTONIETTA LOI⁴ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie — ²Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, OX1 3PU, Oxford, United Kingdom — ³Lawrence Berkeley National Laboratory, Berkeley, California, US — ⁴Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands

Do pre-existing models hold? Or do we need novel approaches to fully understand perovskite photoluminescence?