

CPP 27: Focus Session: When theory meets experiment: Hybrid halide perovskites for applications beyond solar II (joint session HL/CPP)

Hybrid halide perovskites are by now well established solar absorber and emitter materials, with power conversion efficiencies of single cell devices exceeding 20

Organizers: Linn Leppert (Universität Bayreuth) and Felix Deschler (TU Munich)

Time: Monday 15:00–17:00

Location: POT 251

Invited Talk

CPP 27.1 Mon 15:00 POT 251

Double perovskite electronic structures: A chemical perspective — ●ADAM SLAVNEY¹, HEMAMALA KARUNADASA², LINN LEPPERT³, and BRIDGET CONNOR² — ¹Department of Chemistry, Harvard University, Cambridge, Massachusetts, USA — ²Department of Chemistry, Stanford University, Stanford, California, USA — ³Institute of Physics, University of Bayreuth, Bayreuth, Germany

Halide double perovskites, of the formula $A_2BB'X_6$, are close analogs to the $APbX_3$ lead halide perovskites and have attracted significant interest as possible non-toxic alternatives to the lead materials in perovskite photovoltaics. Double perovskites divide the formally +2 charge on the octahedral B site unevenly over two B sites, allowing for cations with charges from +1 - +4 to be incorporated into the perovskite lattice. I will discuss the results of our experimental and theoretical investigations into double perovskites over the last several years, with a particular emphasis on understanding the differences in electronic structure between single and double perovskites. The double perovskite electronic structure is largely dictated by the combination of the B and B* cations rather than either cation individually and I will provide simple rules which accurately predict the band structure from the chemical formula in nearly every case. Double perovskites electronic structures have features not available in single perovskites including symmetry-forbidden bandgaps and unusually small bandgaps generated by metal-metal charge transfer transitions. Finally, I will discuss some of the defect chemistry of double perovskites and how those lessons can be applied to halide perovskites more broadly.

Invited Talk

CPP 27.2 Mon 15:30 POT 251

Solid state ionics of hybrid halide perovskites: equilibrium situation and light effects — ●ALESSANDRO SENOCRATE^{1,2}, GEE YEONG KIM¹, TAE YOUL YANG¹, GIULIANO GREGORI¹, MICHAEL GRAETZEL^{1,2}, and JOACHIM MAIER¹ — ¹Max Planck Institute for Solid State Research, Stuttgart, Germany — ²École polytechnique fédérale de Lausanne

In recent years, hybrid halide perovskites have been attracting great attention due to their exceptional photo-electrochemical properties. When used as light-harvesters in solar cells, device efficiencies exceeding 25% can be realized. We showed that a deeper understanding of (i) functionality, (ii) stability, as well as (iii) the possibility to improve the performance require a thorough insight into non-stoichiometry and ion transport.

In this contribution, we study the nature of the ionic conductivity in methylammonium lead iodide ($MAPbI_3$), the archetypal halide perovskite, by means of a great number of electrochemical and nuclear magnetic techniques. To aid the experimental investigation, we include detailed defect chemical modelling describing the effects of varying iodine partial pressure (stoichiometry) and dopant content. By extending this study to the situation under illumination, we observe a striking enhancement of ionic conductivity by more than 2 orders of magnitude in $MAPbI_3$, alongside the expected increase in electronic conductivity. We provide a mechanistic explanation of this astonishing phenomenon and discuss its relevance for the photo-stability of this class of materials.

CPP 27.3 Mon 16:00 POT 251

Looking beyond the surface: The band gap of bulk methylammonium lead iodide — OSKAR SCHUSTER¹, PETER WIENTJES¹, SHREETA SHRESTHA², IEVGEN LEVCHUK², MYKHAILO SYTNYK³, GEBHARD MATT², ANDRES OSVET², MIROSLAW BATENTSCHUK², WOLFGANG HEISS³, CHRISTOPH BRABEC², THOMAS FAUSTER¹, and ●DANIEL NIESNER¹ — ¹Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Staudtstr. 7, 91058 Erlangen, Germany — ²Materials Science Department (I-MEET), FAU, Martensstrasse 7, 91058 Erlangen, Germany — ³Materials Science Department, FAU, Energy Campus Nürnberg, 90429 Nürnberg, Germany

Reported optical properties of lead halide perovskites as basic as the absorption onset and the band gap vary significantly. To unambiguously answer the question whether the discrepancies are a result of differences between bulk and "near-surface" material, we perform bulk-sensitive two-photon absorption with an information depth in the millimeter range on single crystals. In the application-relevant room-temperature tetragonal phase (170 K) we find a bulk band gap of 1.55 ± 0.01 eV. Reference measurements on the surface-near region in a reflection geometry show excitonic transitions at 1.59 ± 0.01 eV, consistent with the literature. The small band gap of the bulk material explains the extended infrared absorption of crystalline perovskite solar cells, the narrow bandwidth of crystalline perovskite photodetectors making use of the spectral filtering at the surface, and the low-energy bands which carry optically driven spin-polarized currents.

CPP 27.4 Mon 16:15 POT 251

Double Peak Emission in Lead Halide Perovskites by Self-Absorption — ●KONSTANTIN SCHÖTZ¹, ABDELRAHMAN M. ASKAR², WEI PENG³, DOMINIK SEEBERGER¹, TANAJI P. GUJAR¹, MUKUNDAN THELAKKAT¹, SVEN HUETTNER¹, OSMAN M. BAKR³, KARTHIK SHANKAR², ANNA KÖHLER¹, and FABIAN PANZER¹ — ¹Universität Bayreuth, Bayreuth, Germany — ²University of Alberta, Edmonton, Canada — ³King Abdullah University of Science and Technology (KAUST), Thuwal, Kingdom of Saudi Arabia

Despite the rapidly increasing efficiencies of perovskite solar cells, the optoelectronic properties of this material class are not completely understood. Especially when measured photoluminescence (PL) spectra consist of multiple peaks, their origin is still debated. In this work, we investigate in detail double peak PL spectra of halide perovskite thin films and single crystals with different material compositions. By different optical spectroscopic approaches and quantitative models, we demonstrate that the additional PL peak results from an extensive self-absorption effect, whose impact is intensified by strong internal reflections. This self-absorption accounts for the unusual temperature dependence of the additional PL peak and it implies that absorption until far into the Urbach tail of the perovskite is important. The strong internal reflections entail that even for thin films self-absorption can have a significant contribution to the PL spectrum. Our results allow for a clear assignment of the PL peaks by differentiating between optical effects and actual electronic transitions, which is necessary for understanding the optoelectronic properties of halide perovskites.

CPP 27.5 Mon 16:30 POT 251

Surface atomic and electronic structure of $CsPbBr_3$ inorganic perovskite — ●JANEK RIEGER, FELIX TRUNK, THOMAS FAUSTER, and DANIEL NIESNER — Lehrstuhl für Festkörperphysik, Friedrich-Alexander University Erlangen-Nürnberg (FAU), Staudtstr. 7, D-91058 Erlangen, Germany

The crystallographic orientation of the surface has a strong impact on the performance of solar cells built from lead-halide perovskites [1]. For a systematic study of the surface carrier-dynamics, we prepare atomically well-defined (001) surfaces of the inorganic perovskite $CsPbBr_3$ by epitaxial growth in ultra-high vacuum. Low-energy electron diffraction was carried out to analyze the resulting samples.

The measured surface unit cell as well as the corresponding phase transitions differ from the bulk-terminated ones. Angle-resolved photoelectron spectroscopy finds a valence-band structure in line with data we obtained from single crystals. Finally, we also investigated the energetics of the conduction-band electrons using two-photon photoelectron spectroscopy. From the positions of the valence-band maximum and the conduction-band minimum we conclude that our $CsPbBr_3$ samples are intrinsic.

[1] S. Y. Leblebici et al., Nat. Energy **1**, 16093 (2016).

CPP 27.6 Mon 16:45 POT 251

Finite temperature effects on the excited states in layered

BiI₃ — •IVONA BRAVIC and BARTOMEU MONSERRAT — TCM Group, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom

Over the last decade layered BiI₃ has been matter of investigation in the optoelectronics community as it exhibits a fundamental band gap similar to that of silicon but behaves like a direct band gap semiconductor. However, the excited state properties of this system remained poorly understood, which is mostly a consequence of the extremely flat band structure and the arising low robustness with respect to dynamical distortions, volume expansion and stacking faults. In or-

der to determine its potential performance in an optoelectronic device at finite temperature, it proves invaluable to establish a fundamental understanding of its excited states and how the aforementioned properties effect those. In this study we reveal the effect of spin-orbit coupling, electron-phonon coupling, exciton-phonon coupling, stacking faults and volume expansion on the optical response and photoluminescence properties of this materials using DFT as well as GW-BSE, proving that it is crucial to account for all these effects to provide a comprehensive understanding of the optoelectronic performance of layered BiI₃, and in general layered van-der Waals materials.