

CPP 33: Perovskite and photovoltaics II (joint session HL/CPP)

Time: Wednesday 9:30–13:00

Location: POT 251

Invited Talk

CPP 33.1 Wed 9:30 POT 251

Interfaces in perovskite optoelectronics: role of energy level alignment and interface chemistry — ●SELINA OLTHOF — Universität zu Köln, Institut für Physikalische Chemie

Optoelectronic devices, such as perovskite solar cells, are typically multi-layer stacks in which the absorber layer is sandwiched between metal oxide and/or organic transport layers in order to facilitate charge extraction or ensure charge selectivity. As the perovskite absorber layer has been extensively optimized in the past years, the awareness is rising that device efficiency and stability is limited by the interfaces present in the device. However, in perovskite-based devices, the role of this energy level alignment remains to be elusive and rather inconclusive studies can be found in literature, which I will briefly outline. More important for the device seems to be the perovskite composition at the interface which can be significantly influenced by chemical reactions taking place, in particular next to metal oxides. I will summarize our work on a variety of metal oxides in which we use photoelectron spectroscopy to analyze which components are responsible for the strong interface chemistry. We show that the reactivity strongly depends on the choice of perovskite and that different metal oxides show fundamentally different reaction/degradation pathways. Intriguingly, we are able to introduce surface treatments which change the surface defect density and thereby affect the degree of perovskite degradation significantly.

CPP 33.2 Wed 10:00 POT 251

Silver-nanoclusters and -vacancies influence the optical properties of Cs₂AgBiCl₆ nanocrystals — ●FEI HE¹, YIYOU WANG¹, QUINTEN A. AKKERMAN¹, MARKUS DÖBLINGER², AMRITA DEY¹, and JOCHEN FELDMANN¹ — ¹Chair for Photonics and Optoelectronics, Nano-Institute Munich and Department of Physics, Ludwig-Maximilians-Universität, Königinstraße 10, 80539 Munich, Germany — ²Department of Chemistry, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (E), 81377 München, Germany

Though being indirect semiconductors Cesium-Silver-Bismuth-Halides (so-called double perovskites) have attracted much attention as a non-toxic alternative to Lead Halide Perovskites. Novel applications for solar cells and X-ray detectors have already been developed.

Here, we report on the successful synthesis of spherical Cs₂AgBiCl₆ nanocrystals showing good stability and characteristic photoluminescent spectra. In transmission electron microscopy (TEM) images we observe Ag-clusters on the surface of the nanocrystals. It is known that silver ions are easily reduced into metallic Ag leading to silver vacancies in the double perovskite material and probably to Ag-clusters on the surface. We discuss how silver-nanoclusters and -vacancies influence the luminescent behavior of the double perovskite nanocrystals and explain possible microscopic origins.

CPP 33.3 Wed 10:15 POT 251

Accelerating research on solar cell materials with NOMAD — ●JOSE MARQUEZ¹, LAURI HIMANEN¹, MARKUS SCHEIDGEN¹, CLAUDIA DRAXL¹, JENS HAUCH², CHRISTOPH BRABEC², and THOMAS ERNOLD³ — ¹Humboldt Universität zu Berlin — ²Helmholtz Institute Erlangen-Nürnberg for Renewable Energy — ³Helmholtz-Zentrum Berlin

New solar cell technologies need decades to overcome the 20% power conversion efficiency threshold needed to make them commercially viable. With thousands of possible chemical compositions for new absorber layer materials and an unlimited number of possible device architectures, it becomes impossible to navigate this material space without the help of data science. To radically accelerate and democratize this development process, FAIR data management activities involving experimental solar cell data are needed. The NOMAD Laboratory (<https://nomad-lab.eu>) is a platform and open-source software driven by the NFDI consortium FAIRmat (<https://fairmat-nfdi.eu>) for making materials-science data FAIR. We show how the NOMAD infrastructure is evolving to support this task in the context of solar cells, demonstrated by an app for visualizing and searching rich and AI-ready experimental big solar cell data. NOMAD also provides an electronic lab notebook (ELN) which can be customized by research labs for AI-ready data/metadata entry, transfer, and processing in a FAIR-database context.

CPP 33.4 Wed 10:30 POT 251

Interdiffusion of Cu(In,Ga)Se₂ and Ag(In,Ga)Se₂ investigated by In-Situ X-Ray Diffraction — ●JULIA HORSTMANN¹, ROLAND MAINZ², KARSTEN ALBE³, HEIKO KEMPA¹, TORSTEN HÖLSCHER¹, and ROLAND SCHEER¹ — ¹Martin-Luther-Universität Halle-Wittenberg, Germany — ²Helmholtz-Zentrum Berlin, Germany — ³Technische Universität Darmstadt, Germany

The partial substitution of Ag with Cu in the chalcopyrite-based absorber of thin film solar cells is a promising approach towards higher power conversion efficiencies. The resulting (Ag,Cu)(In,Ga)Se₂ (ACIGSe) alloy achieves a bandgap widening up to 0.2 eV, increased grain growth and a lower melting temperature. The latter might reduce structural defects and therefore recombination losses in the absorber. This is favorable especially for wide-bandgap solar cells, used as top subcells in tandem devices, whose device performance is mainly limited by deep defects. To gain a better understanding of the diffusion on the (I) sublattice, we experimentally explored the interdiffusion of Cu(In,Ga)Se₂ and Ag(In,Ga)Se₂ layers by in-situ X-ray diffraction (IS-XRD) and glow discharge optical emission spectroscopy. Besides the positive aspects of Ag-alloying, thermodynamic simulations have shown a miscibility gap for temperatures between 100°C and 400°C. It is theoretically proposed, that ACIGSe with a high Ga content and with a [Ag]/([Ag]+[Cu]) ratio between 0.25 and 0.75 decomposes into Ag-rich and Ag-poor phases. We have studied the phase stability of Ga-free and Ga-rich samples using IS-XRD during post-annealing processes.

CPP 33.5 Wed 10:45 POT 251

NiO in perovskite solar cells: a peculiar interplay of degradation, passivation and device performance — ●JOHN MOHANRAJ¹, BIPASA SAMANTA², MAYTAL CASPARY TOROKAR², and SELINA OLTHOF¹ — ¹University of Cologne, 50939 Cologne, Germany — ²Technion - IIT, Haifa, 3200003 Israel

The degradative interactions at the NiO/perovskite interface are notorious in the perovskite community as they lead to significant Voc and stability losses in p-i-n type perovskite solar cells (PSCs). So far, various Lewis bases have been introduced at this interface to passivate the metal oxide surface defects. Despite this process being successful in minimizing Voc and stability losses in PSCs, in-depth understanding of surface passivation and consequent suppression of the chemical processes at the NiO/perovskite interface are still elusive. This calls for a comprehensive surface investigation. To address these issues, we investigated solution processed NiO surfaces, their treatment with a series of passivating compounds, and the interface towards MAPbI₃ in order to systematically probe the interface stability. Our methods include X-ray and UV photoelectron spectroscopy (XPS/UPS), XRD, SEM and UV-Vis absorption techniques. In parallel, first principle DFT calculations on differently treated NiO/MAPbI₃ interfaces were carried out. These complementary investigations reveal changes in surface composition of the treated NiO and help us to suggest possible mechanisms for the degradative interactions. Finally, PSCs were fabricated using the stabilized NiO interfaces, and the impact on photovoltaic characteristics and device stability have been investigated.

30 min. break

CPP 33.6 Wed 11:30 POT 251

Resonant coupling of spin-flip excitations with phonons in BiFeO₃ — ●ASEEM RAJAN KSHIRSAGAR and SVEN REICHARDT — Department of Physics and Material Science, University of Luxembourg, Luxembourg

BiFeO₃ is a technologically relevant multiferroic perovskite. While a vast literature exists on its electronic, optical, and multiferroic properties, some of its optically active electronic excitations remain to be understood or have been interpreted in ambiguous ways. This applies in particular to features below the absorption onset that feature prominently in resonant Raman scattering [1]. Here we present a detailed study of the electronic structure and resonant Raman spectrum of BiFeO₃ from first principles. Using many-body perturbation theory on top of density functional theory, we first analyze and characterize its optical absorption spectrum in terms of excitons and atomic orbitals, focusing in particular on spin-flip excitations that are strongly

localized. We then use the state-of-the-art method for the ab initio calculation of resonant Raman intensities [2,3] to analyze the resonant coupling of these finite-spin excitations with phonons. Our results show that these only weakly optically active excitations still leave a clear imprint on the resonant Raman spectrum, making the latter an even more powerful tool to probe "darker" electronic excitations.

- [1] M. C. Weber, et al. Phys. Rev. B, 93, 125204 (2016).
 [2] S. Reichardt and L. Wirtz, Phys. Rev. B, 99, 174312 (2019).
 [3] S. Reichardt and L. Wirtz, Sci. Adv., 6, eabb5915 (2020).

CPP 33.7 Wed 11:45 POT 251

Coherent Phonons in Halide Perovskite Nanocrystals — ●JULIAN GEORG MANN¹, FEI HE¹, QUINTEN AKKERMAN¹, TUSHAR DEBNATH², and JOCHEN FELDMANN¹ — ¹Chair for Photonics and Optoelectronics, Nano-Institute Munich and Department of Physics, Ludwig-Maximilians-Universität (LMU), Königinstr. 10, 80539 Munich, Germany — ²Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati-781039

Halide perovskite nanocrystals are gaining increasing attention in contemporary research due to their promising performance in both light-emitting and solar technologies. We recently showed that photoexcitation of halide-perovskite nanocrystals with ultrashort laser pulses produces coherent phonons (Nat. Comm. 12, 2629 (2021)). We report femtosecond pump-probe spectroscopy studies on the formation and dynamics of coherent phonons in formamidinium lead-halide (FAPbX₃) nanocrystals in terms of higher harmonic vibrational modes. In addition, we investigate the dynamics of vibrational wave packets in spherical Cs₂AgBiBr₆ double perovskite nanocrystals. Here, we observe that optically launched vibrational wave-packets alter spectral positions of excitonic resonances or oscillator strength of particular electronic transitions. Our results show that electron-phonon couplings (polaronic effects) need to be considered to fully understand the optoelectronic properties of halide-perovskite semiconductors.

CPP 33.8 Wed 12:00 POT 251

Phonon-driven Intra-exciton Rabi Oscillations in Halide Perovskites — ●KATRIN WINTE¹, XUAN TRUNG NGUYEN¹, DANIEL TIMMER¹, DAVIDE CERATTI², CATERINA COCCHI¹, MICHAEL LOREK³, FRANK JAHNKE³, DAVID CAHEN², CHRISTOPH LIENAU¹, and ANTONIETTA DE SIO¹ — ¹University of Oldenburg, Germany — ²Weizmann Institute of Science, Israel — ³University of Bremen, Germany

There is increasing consensus that in halide perovskites (HaPs) the interaction of electronic excitations with the phonon modes of their flexible polar lattice is crucial for the unique optoelectronic and transport properties of these materials. Here we show that coherent low frequency phonon of the lead-halide lattice induce Rabi oscillations between 1s and 2p excitons in CsPbBr₃ crystals. Ultrafast two-dimensional electronic spectroscopy reveals an excitonic peak structure oscillating with a 100-fs period up to 2 ps at 20 K. This frequency does not match any phonon modes of the crystals. Only after 2 ps, slow coherent phonon oscillations dominate the dynamics. We rationalize these findings as off-resonant intra-exciton Rabi oscillations induced by the Pb-Br phonon fields of the HaP crystals. We show that the slow motion of Pb-Br sublattice induces electric fields at THz frequencies that are sufficiently strong to drive off-resonant population oscillations between 1s and 2s excitons. Model simulation of the nonlinear optical response support this interpretation. This goes beyond prevailing models for the electron-phonon coupling in HaPs. It suggests that the coupling of characteristic low frequency phonon to intra-excitonic transitions may be the key to control their anharmonic response.

CPP 33.9 Wed 12:15 POT 251

Determining (almost) all optoelectronic properties of halide perovskites by transient photoluminescence — ●HANNES HEMPEL¹, MARTIN STOLTERFOHT², FANGYUAN YE², and THOMAS UNOLD¹ — ¹Helmholtz Zentrum Berlin, Germany — ²Institute of Physics and Astronomy, University of Potsdam, Germany

Time-resolved photo luminescence (trPL) is probably the most common technique to quantify lifetimes of photogenerated charge carriers in semiconductors. However, the usual fitting of exponential decays to

estimate lifetimes is a rather crude phenomenological approach since it ignores quenching processes that are not connected to carrier recombination and disregards the absolute amplitude of the luminescence. Here, we present an analysis of injection-dependent absolute trPL transients of bare triple-cation lead halide perovskite thin films. The presented analysis reveals a doping concentration of 3x10¹³cm⁻³ and a charge carrier mobility of 0.8 cm²/Vs, which are confirmed by Hall measurements. Further, we determine the injection-dependence of external radiative lifetimes, of the external radiative coefficient, and of the effective charge carrier lifetime. Based on the properties, an implied current-voltage curve is constructed that reveals the potential performance of the material in solar cell. Our trPL-based approach agrees well with the results of injection-dependent photoluminescence quantum yield measurements. However, it is superior in attributing losses, e.g. in the radiative ideality factor or the implied open circuit voltage, to the internal optoelectronic properties and thereby indicates the path to overcome these losses.

CPP 33.10 Wed 12:30 POT 251

Characterization of optoelectronic properties of CsSnI₃ perovskite thin film as a function of chemical composition. — ●FATIMA AKHUNDOVA, HANNES HEMPEL, MARIN RUSU, ELIF HÜSAM, MARCUS BÄR, and THOMAS UNOLD — Helmholtz-Zentrum Berlin

The performance of lead-based halide perovskites as a next generation solar cell rises every year, however toxicity of Pb is a major obstacle for commercialization. Tin is the immediate substitute for Pb in perovskite crystal structure as both metals possess the same electronic configuration. However, Sn-perovskite solar cells have significantly lower efficiencies which is partially caused by poor stability of Sn(II). We report a systematic study of structural and optoelectronic properties of co-evaporated CsSnI₃ thin films with regard to lateral compositional gradient. Elemental compositions are confirmed by X-ray fluorescence and X-ray photoelectron spectroscopy techniques. Grazing-incidence X-ray diffraction reveals orthorhombic gamma phase with different preferred orientation for the excess Sn and Cs content. Moreover, Cs-rich regions shows better phase stability than the Sn-rich parts which undergo a phase transition to non-perovskite phase. The optical band gap, work function, and ionization energy are measured as a function of the Cs:Sn ratio to characterize the band diagram. The photoluminescence quantum yield, the charge carrier lifetime and mobility present these properties are rather robust against changes in composition. Our work emphasizes the impact of chemical composition on optoelectronic properties of Sn-based perovskites and demonstrates agile strategy for compositional engineering in materials research.

CPP 33.11 Wed 12:45 POT 251

FAIR Cesium Lead Halide Perovskites Data by High-Throughput Investigation of Co-Evaporated Combinatorial Libraries — ●HAMPUS NÄSSTRÖM¹, PASCAL BEBLO², FATIMA AKHUNDOVA², OLEKSANDRA SHARGAIEVA², JOSE A. MARQUEZ¹, HANNES HEMPEL², ANDREA ALBINO¹, SEBASTIAN BRÜCKNER¹, CLAUDIA DRAXL¹, EVA UNGER², and THOMAS UNOLD² — ¹Humboldt-Universität zu Berlin — ²Helmholtz-Zentrum Berlin

Artificial intelligence presents new possibilities in experimental materials research but typically require large well-characterized datasets. High-throughput technologies, including combinatorial synthesis, provide one method for obtaining such datasets. In this work, we show how such a dataset can be created through combinatorial co-evaporation and high-throughput characterization of Cs_yPb_{1-y}(Br_xI_{1-x})_{2-y} perovskites. The evaporated films were investigated with a multitude of contact-less characterization methods such as hyperspectral photoluminescence imaging, time-resolved photoluminescence mapping, and grazing-incidence wide-angle X-ray scattering mapping. The results were combined to estimate the potential of the material in terms of the photovoltaic power conversion efficiency as a function of the Cs to Pb and Br to I ratio. Finally, a generalized data schema for combinatorial thin films was developed, and the data of the 3456 individual samples was disseminated in a Findable, Accessible, Interoperable and Reusable (FAIR) way within the Novel Materials Discovery (NOMAD) laboratory (nomad-lab.eu) that is operated by the NFDI consortium FAIRmat (fairmat-nfdi.eu).