

KFM 22: Perovskite and Photovoltaics II (joint session HL/KFM)

Time: Thursday 9:30–13:15

Location: EW 203

KFM 22.1 Thu 9:30 EW 203

Raman spectroscopy on BaTiS₃ perovskite nanocrystals — ●SELINA NÖCKER¹, SANDRA ZECH¹, VINCENT MAURITZ², KATHARINA DEHM², RYAN CRISP², and JANINA MAULTZSCH¹ — ¹Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — ²Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Perovskites and related materials are emerging candidates for photovoltaics demonstrating promising energy conversion efficiencies. Here we study lead- and halide-free BaTiS₃, colloiddally synthesized as wire- and rod-shaped nanocrystals.

For the structural analysis of those nanocrystals, we use Raman spectroscopy and compare the results to single-crystal spectra of BaTiS₃. Our study includes temperature-dependent and excitation-wavelength dependent measurements. Moreover, we show that Raman spectroscopy can be used as a straightforward method to distinguish between the two shape types.

KFM 22.2 Thu 9:45 EW 203

Crystallization and defect properties in combinatorially synthesized BaZrS₃ thin films — ●ADRIANA RÖTTGER¹, JACK VAN SAMBEEK², MARIN RUSU¹, HANNES HEMPEL¹, RAFAEL JARAMILLO², and THOMAS UNOLD¹ — ¹Helmholtz-Zentrum Berlin, Deutschland — ²Massachusetts Institute of Technology, Cambridge, MA, USA

BaZrS₃ is a chalcogenide perovskite composed of Earth-abundant elements with potential applications for photovoltaic (PV) energy conversion. Using pulsed laser deposition, oxide precursors with a lateral [Ba]/[Zr] ratio, ranging from 0.8 to 1.3, were deposited on 50 x 12 mm² large samples, which were then sulfurized in a tube furnace using different concentrations of H₂S in Ar gas at temperatures ranging from 800°C to 1000°C. The combinatorial nature of the thin films allows the study of crystallization behavior dependent on the composition of the material. A considerable increase in crystallite size was observed from the Zr-rich side to the Ba-rich side of all samples using grazing incidence x-ray diffraction and scanning electron microscopy. We hypothesize that Ba excess leads to liquid phase assisted growth, similar to a low temperature growth mechanism reported recently by Yang et al.^[1] We demonstrate control over the kinetics of crystallization by varying temperature and/or H₂S partial pressure. We find that band-edge photoluminescence (PL) increases from the Ba-rich to the Zr-rich side, while defect state PL probed at low temperatures show a reverse trend. This suggests that careful control of the metals ratio will be key to achieving thin films with large crystals and good PV performance. [1] Yang et al., *Chemistry of Materials* 2023 35 (12), 4743-4750

KFM 22.3 Thu 10:00 EW 203

Combining transient photoluminescence and transient surface photovoltage experiments: insights from drift-diffusion modeling — ●ORESTIS KARALIS, HANNES HEMPEL, and THOMAS UNOLD — Helmholtz-Zentrum Berlin, Berlin, Deutschland

The combination of transient surface photovoltage (trSPV) and transient photoluminescence (trPL) can help to distinguish charge transfer and recombination at the interfaces between photo-absorbers and charge-selective layers (I. Levine, 2021). This distinction is particularly crucial for the optimization of halide perovskite solar cells, as their power conversion efficiency is mainly limited by interfacial losses. However rate-equation models previously employed for trSPV (I. Levine, 2021) or trPL (F. Staub, 2016) are unable to simultaneously describe both experiments, which raises concerns about the validity of their findings. To address this limitation, we perform drift-diffusion modeling utilizing the open-source SIMsalabim algorithm (M. Koopmans, 2022). Our investigation reveals that strong charging of the sample with repetitive pulsed illumination, a factor overlooked in previous models, can strongly change the shape of the transients. Based on the improved model, we explore the impact of various parameters, such as charge-transfer velocity, bulk trap density, energy level alignment between absorber and charge transport layer, on the trPL and trSPV transients, as well as on overall solar cell performance. Finally, comparison of these simulations allows a simple phenomenological interpretation of trPL and trSPV. This insight can serve as a valuable guide in the pursuit of optimizing halide perovskite solar cells.

KFM 22.4 Thu 10:15 EW 203

Impact of different substrates and annealing treatments on the formation of fully evaporated perovskite — ●MOHAMED MAHMOUD^{1,2}, MARTIN BIVOUR¹, YASHIKA GUPTA^{1,2}, OUSSAMA ERAJJI^{1,2}, and JULIANE BORCHERT^{1,2} — ¹Fraunhofer ISE, Freiburg, Germany — ²University of Freiburg, Freiburg, Germany

Perovskite solar cells have the advantages of a strong absorption edge, defect tolerance, and potential cheap production. In the industry, a great interest is shown towards perovskite-silicon tandem solar cells to overcome the single junction limit. Double-sided textured (micrometer sized pyramid) silicon is commonly produced to decrease reflection losses and improve light trapping. Solution-based processing methods of perovskite on top of the textured silicon showed low conformality, which resulted in shunts and non-working solar cells. To overcome this issue, physical vapor deposition (PVD) is used for the different precursors to conformally coat the perovskite on the silicon pyramids. Therefore, we study distinct vacuum-based methodologies for perovskite processing, specifically the hybrid route and the fully evaporated route. In this study, we investigate the effect of different substrates, that includes different materials and different Si pyramid heights, on the formation of fully evaporated perovskite. The results show that different surfaces (i.e. different materials) affects not only the morphology of the evaporated perovskite, but also the crystal structure. In addition to that, we compare planar Si surfaces to nano structured as well as micro structured on the formation of fully evaporated perovskite.

KFM 22.5 Thu 10:30 EW 203

Room temperature exciton-polaritons in quasi-2D Ruddlesden-Popper perovskites — ●HAMID PASHAEI ADL^{1,2}, CHRISTOPH BENNEHEI¹, JENS CHRISTIAN DRAWER¹, LUKAS LACKNER¹, MARTI STRUVE¹, ANTHONY ERNZERHOF¹, NADIYA MATUKHNO¹, SIGALIT AHARON³, DAVID CAHEN³, MARTIN ESMANN¹, and CHRISTIAN SCHNEIDER¹ — ¹Institute for Physics, Carl von Ossietzky University of Oldenburg, 26129 Oldenburg, Germany. — ²Instituto de Ciencia de Materiales (ICMUV) Universidad de Valencia/Catedrático José Beltrán, 2, Paterna E-46980, Spain. — ³Weizmann Institute of Science 234 Herzl Street, Rehovot 7610001, Israel.

Ruddlesden-Popper (RP) layered perovskites [1] with high oscillator strength and large exciton binding energy are promising materials for photonic applications. The crystalline form of these perovskites can be used as excitonic medium in optical microcavities, allowing for the study of their optical properties in the strong light-matter coupling regime. Here, using angle resolved reflection spectroscopy, we show tunable strong coupling of light modes to mechanically exfoliated quasi-2D RP flakes in an open access microcavity under ambient conditions [2], which is supported by transfer matrix calculations. In ongoing experiments, we introduce structured photonic lattices to the open cavity to study the coupling of the polaritons to tailored topological features and investigate Bose-Einstein condensation.

[1] J. C. Blancon, et al., *Nat Nanotechnology* 15, 969 (2020). [2] L. Lackner, et al., *Nat Commun* 12, 4933 (2021).

KFM 22.6 Thu 10:45 EW 203

Predicting Optoelectronic Performance: A First-Principles Analysis of Carrier Recombination in Metal Halide Perovskites — UTKARSH SINGH and ●SERGEI I. SIMAK — Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83, Linköping, Sweden

Unveiling the full potential of Metal Halide perovskites (MHPs) for optoelectronic applications depends on understanding factors influencing device performance, specifically the interplay between radiative and non-radiative recombination at various carrier densities. We explore these processes, laying the foundation for enhanced device functionality and tailored design approaches. We implement the calculation of carrier recombination facilitated through direct and phonon-assisted mechanisms via a first-principles approach. Using methods at and beyond the level of density functional theory, we highlight the role of MHP constituents and the contribution of various factors towards carrier dynamics. The primary focus is on MHPs CsPbI₃ and its lead-free counterpart CsSnI₃, where high radiative and low non-radiative

recombination rates are favorable for potential use as LEDs. We reveal how these processes depend on the material's electronic structure, dictating the phase space available for charge carrier interactions [1]. An in-depth understanding of principles governing recombination dynamics, implemented in a predictive framework, may significantly impact advancements in this field.

[1] F. Yuan et al., "Bright and stable near-infrared lead-free perovskite light-emitting diodes", *Nature Photonics* (2023, accepted).

KFM 22.7 Thu 11:00 EW 203

Additive engineering for high bandgap perovskite absorber for application in triple-junction solar cells — ●ATHIRA SHAJI¹, MINASADAT HEYDARIAN¹, MARYAMSADAT HEYDARIAN¹, PATRICIA S. C. SCHULZE¹, JULIANE BORCHERT^{1,2}, and ANDREAS BETT¹ — ¹Fraunhofer Institute for Solar Energy Systems — ²INATECH, University of Freiburg

Multi-junction solar cells can overcome the theoretical efficiency limit of state-of-the-art silicon single-junction solar cell. Recently, perovskite-silicon tandem solar cells have achieved high power conversion efficiency (PCE) of 33.9% on small area. By adding a third junction this PCE can be further increased. For a top cell in a triple-junction solar cell, a high band gap (HBG) perovskite is required. However, there are several challenges associated with such HBG perovskites such as photo-induced phase segregation and high V_{OC} deficit¹. In addition, the high Br content in the HBG perovskite composition has been lead to poor perovskite film formation and morphology which can exacerbate the mentioned issues¹. Suppression of phase segregation and increased grain size can be achieved by improving the perovskite crystallization via additive engineering¹. Here, we employ a triple cation perovskite composition with general formula $Cs_{0.05}(FA_{1-x}MA_x)_{0.95}Pb(I_{1-x}Br_x)_3$ ($E_g > 1.83$ eV) which is used as the top cell absorber². We investigate the effects of additives on this perovskite crystallization and grain size¹.

1.Chen, B. et al. *Joule* 2019, 3(1), 177-190.

2.Heydarian, M. et al. *ACS Energy Lett.* 2023, 8(10), 4186-4192.

15 min. break

KFM 22.8 Thu 11:30 EW 203

Thermodynamics and kinetics of silver in Cu(In,Ga)Se₂ solar cell absorbers — MARKUS MOCK, ●DELWIN PERERA, and KARSTEN ALBE — Institut für Materialwissenschaft, Technische Universität Darmstadt, Germany

Cu(In,Ga)Se₂ (CIGS) is at the moment the most efficient absorber material in thin-film solar cells. Its efficiency can be further enhanced by substituting copper with silver which increases the band gap and turns CIGS into a wide-gap semiconductor with potential application in tandem solar cells.

In this contribution, we investigate the impact of silver on structural and electronic properties of CIGS. Using semi-grand canonical Monte Carlo simulations, we explore the CIGS phase diagram as a function of silver content. In particular, we map out the phase transition between solid solution and phase decomposition as well as the spinodal region. Based on a cluster expansion model, our Monte Carlo simulations reveal the microstructure evolution within the binodal region. We supplement the thermodynamic analysis with kinetic considerations by calculating defect migration barriers and defect association energies. Finally, we investigate the effect of silver on the band gap employing hybrid density functional theory calculations.

KFM 22.9 Thu 11:45 EW 203

Photon echo spectroscopy of CsPbI₃ nanocrystals — ARTUR V. TRIFONOV^{1,2}, ●MARIO ALEX HOLLBERG¹, STEFAN GRISARD¹, ELENA V. KOLOBKOVA^{3,4}, MARIA S. KUZNETSOV², MIKHAIL O. NESTOKLON¹, JAN KASPARI⁵, DORIS REITER⁵, DMITRI R. YAKOVLEV^{1,6}, MANFRED BAYER¹, and ILYA A. AKIMOV¹ — ¹Experimentelle Physik 2, Technische Universität Dortmund — ²St. Petersburg, Russia — ³St. Petersburg, Russia — ⁴St. Petersburg, Russia — ⁵Condensed Matter Theory, Technische Universität Dortmund — ⁶St. Petersburg, Russia

All-inorganic halide perovskite nanocrystals hold potential for future optoelectronic technologies. One of the paths to fully unlock their capabilities, is a deeper understanding of coherent exciton dynamics in these materials. In this work, we investigated a caesium lead tri-iodide (CsPbI₃) nanocrystal ensemble using time-resolved photon echo spectroscopy at cryogenic temperatures (1.5 K). We observed a long exciton

lifetime T_1 of about 1 ns and an exciton coherence time T_2 of up to approximately 300 ps. The initial tens of picoseconds in the photon echo decay exhibited oscillatory behavior with two most pronounced frequencies of 3.2 meV and 5.1 meV, which we attribute to the interaction between excitons and optical phonons. The exciton fine structure manifests itself at lower oscillation frequencies of 0.2 meV and 1.1 meV.

KFM 22.10 Thu 12:00 EW 203

Damping the phase segregation in mixed halide perovskites: Influence of X-site anion — ●MARIA AZHAR — Universitz of Konstanz, Konstanz, Germany

This study reveals that phase segregation becomes more prominent on decreasing bromine content in mixed halide CsPbBr_{3-x}Cl_x perovskites, when bromine content is 50NCs have been synthesized to mitigate the phase segregation. The grain size of the synthesized NCs exists in the range of 20*25 nm. The selected area electron diffraction exhibits the faint rings of the CsPbBr_{1.5}Cl_{1.5} indicating the presence of defects in NCs and the X-rays diffraction analysis confirms the NCs exist in monoclinic crystal structure. Mixed halides perovskites have same crystal structure but exhibit a slight shift in 2θ values. The trend in stability follows the order as, CsPbBr_{3-x}Cl_x > CsPbCl₃ > CsPbBr₃ that is estimated by the values of octahedral factor (μ) and tolerance factor (t). The UV*Vis and steady-state photoluminescence (PL) analysis depict a blue-shift in the spectra by substituting bromine with chlorine in CsPbBr₃. The PL kinetics analysis predicts the CsPbBr_{2.5}Cl_{0.5} exhibits the longest average PL lifetime amongst all other CsPbBr_{3-x}Cl_x perovskites NCs. Our study provides insights in designing stable mixed halides perovskites by suppressing the phase segregation.

KFM 22.11 Thu 12:15 EW 203

Extrinsic doping and compensating defects in the 2D hybrid perovskite PEA₂PbI₄ — GABRIELLE KOKNAT¹, HAIPENG LU^{2,3}, YI YAO¹, JI HAO², XIXI QIN¹, CHUANXIAO XIAO², RUYI SONG¹, FLORIAN MERZ⁴, MARKUS RAMPF⁵, ●SEBASTIAN KOKOTT⁶, CHRISTIAN CARBOGNO⁶, TIANYANG LI¹, GLENN TEETER², MATTHIAS SCHEFFLER⁶, JOSEPH J. BERRY², DAVID B. MITZI¹, JEFFREY L. BLACKBURN², VOLKER BLUM¹, and MATTHEW C. BEARD² — ¹Duke University, Durham, NC, USA — ²NREL, Golden, CO, USA — ³Hong Kong University of Science and Technology, Hong Kong, China — ⁴Lenovo HPC Innovation Center, Stuttgart, Germany — ⁵MPCDF, Garching, Germany — ⁶NOMAD laboratory at FHI, Berlin, Germany

2D hybrid organic-inorganic perovskites are exciting materials for optoelectronic device applications due to their higher chemical and structural adjustability. Precise control over carrier concentrations necessitates the electronic doping of these materials through the incorporation of extrinsic dopants. Conversely, the undesirable presence of intrinsic defects can adversely affect electronic doping efficiencies. In this study, we investigate intrinsic point defects and extrinsic dopants (e.g., Bi, Sn [PRX Energy, 2, 023010 (2023)]) both in isolation and as combined defects in phenylethylammonium lead iodide (PEA₂PbI₄). Employing spin-orbit-coupled hybrid density functional theory (DFT) and supercell models scaling up to 3,383 atoms, we identify the anticipated positions of dopant-derived electronic levels within the bandgap. Complementary experimental findings reinforce hypotheses of compensation mechanisms and limiting factors derived from DFT.

KFM 22.12 Thu 12:30 EW 203

Growth and Investigation of Sequentially Evaporated Mixed Halide (Cs,FA)Pb(I,Br)3 Perovskites — ●TOBIAS SCHULZ¹, KARL HEINZE¹, PAUL PISTOR², and ROLAND SCHEER¹ — ¹Martin-Luther-Universität Halle-Wittenberg, Von-Danckelmann-Platz 3, 06120 Halle (Saale), Germany — ²Universidad de Pablo de Olavide, Carretera de Utrera 1, 41013 Sevilla, Spain

Perovskite films were grown via thermal evaporation and characterized via in situ XRD which give structural information in real-time. Besides the growth of FAPbI₃ and (Cs,FA)PbI₃ also bromine incorporation into the perovskite to prepare (Cs,FA)Pb(I,Br)₃ was investigated [1]. The substitution of iodine with bromine increases the band gap, which is interesting for tandem applications, and improves the thermal stability. In contrast to co-evaporation, the less studied sequential evaporation route was employed which allows a more precise process control. Sequential perovskite formation in vacuum in general proceeds via diffusion of the reactants CsI, FAI, PbI₂, and PbBr₂ which are assembled in different layer stacks. With the in situ XRD setup, the diffusion of these materials during the necessary annealing step was observed. In combination with SEM images, the reactant's diffusion speed was

quantified. Additionally, the perovskites show no unfavourable delta-phase during our experiments, allowing the assumption, that sequential evaporation can fully suppress this non-photoactive phase. [1]: K. Heinze, T. Schulz et al., "Structural Evolution of Sequentially Evaporated (Cs,FA)Pb(I,Br)₃ Perovskite Thin Films via In Situ XRD", *Physica Status Solidi A*, accepted for publication

KFM 22.13 Thu 12:45 EW 203

Impact of ion migration on the performance and stability of perovskite-based tandem solar cells — ●SAHIL SHAH and MARTIN STOLTERFOHT — Physik weicher Materie, Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany

Mobile ions play a significant role in perovskite photovoltaics, yet their impact on the overall performance and stability of tandem solar cells (TSCs) remains largely unexplored. In this study, we present a comprehensive study that combines an experimental analysis of ionic losses in Si/perovskite and all-perovskite TSCs, drift-diffusion simulations, and sub-cell-selective measurements on all-perovskite TSCs during aging. Our findings demonstrate that mobile ions have a significant influence on the hysteresis of Si/perovskite tandem solar cells at high scan speeds (400 V/s) during current-voltage measurements, as well as on performance degradation due to field screening. Additionally, subcell-dominated measurements reveal more pronounced ionic losses in the wide-bandgap subcell during aging, which we attribute to its tendency for halide segregation. Drift-diffusion simulations fully corroborate the results. Overall, this work provides valuable insights into ionic losses in perovskite solar cells and discloses new opportunities for their optimization toward more efficient and stable perovskite-based tandem

cells.

KFM 22.14 Thu 13:00 EW 203

Why copper oxide is not a reliable hole transporting layer for perovskite solar cells — ●MALGORZATA KOT¹, LUDWIG MARTH², ZBIGNIEW STAROWICZ³, PAUL PLATE², JAN INGO FLEGE¹, and KATARZYNA GAWLINSKA-NECEK³ — ¹APhLS, BTU Cottbus-Senftenberg, Konrad-Zuse-Str. 1, 03046 Cottbus, Germany — ²SENTECH INSTRUMENTS GmbH, Schwarzschildstr. 2, 12489 Berlin, Germany — ³IMMS PAS, Photovoltaic Laboratory, 22 Krakowska St., 43-340 Kozy, Poland

One approach, among many others, to increase the stability of perovskite solar cells is to replace an organic hole transporting layer (HTL), which becomes highly unstable when exposed to air for a long time, with more stable inorganic materials. The material that seems to be very promising is copper oxide. In our investigation we however found, that the formamidinium lead iodide perovskite deposited directly on copper oxide in the p-i-n structure degrades within tens of minutes due to the migration of copper ions under X-ray exposure and creation of CuI and Cu. Furthermore, an application of an ultrathin atomic layer deposited Al₂O₃ film on the copper oxide substrate, that in our previous work [1] successively blocked the migration of perovskite ions into the HTL in the n-i-p structure, does not sufficiently block the migration of copper ions through the perovskite film. Therefore, in order for copper oxide to be a reliable HTL for perovskite solar cells, an effective method must be still developed to block the migration of copper ions into other layers. [1] C. Das et al., *Cell Rep. Phys. Sci.* 2020, 100112.