HL 1: Perovskite and Photovoltaics I (joint session HL/KFM)

Time: Monday 9:30–13:00 Location: H13

HL 1.1 Mon 9:30 H13

Oxygen-Mediated (0D) Cs4PbX6 Formation during Open-Air Thermal Processing Improves Inorganic Perovskite Solar Cell Performance — Rafikul Ali Saha[1], •Wei-Hsun Chiu[2], Giedrius Degutis[1], Peng Chen[3], Matthias Filez[4], Eduardo Solano[5], Nikolai Orlov[6], Francesco De Angelis[7], Carlo Meneghini[7], Christophe Detavernier[4], Sawanta S. Mali[8], Minh Tam Hoang[2], Yang Yang[2], Erik C. Garnett[9], Lianzhou Wang[3], Hongxia Wang[2], Maarten B. J. Roeffaers[1], and Julian A. Steele[3] — [1]KU Leuven, Belgium — [2]Queensland University of Technology, Brisbane, Australia — [3]The University of Queensland, Brisbane, Australia — [4]Ghent University, Belgium — [5]ALBA synchrotron, Barcelona, Spain — [6]AMOLF, Amsterdam, The Netherlands — [7]Roma Tre University, Rome, Italy — [8]Chonnam National University, Gwangju, South Korea — [9]University of Amsterdam, The Netherlands

We highlight the beneficial role of ambient oxygen during the open-air thermal processing of metastable γ-CsPbI3-based perovskite thin films and devices. Physiochemical-sensitive probes elucidate oxygen intercalation and the formation of Pb-O bonds in the perovskite, entering via iodine vacancies at the surface, creating superoxide (O2-) through electron transfer reactions, which drives the formation of a zero-dimensional (0D) Cs4PbI6 protective capping layer during annealing (>330°C). Applied to γ-CsPbI2Br perovskite solar cells, it boosts the operational stability and photo-conversion efficiency of champion devices from 12.7% to 15.4% when annealed in dry air.

HL 1.2 Mon 9:45 H13

Compositional Engineering of Mixed-Metal Chalcohalides for Photovoltaic Applications — •Pascal Henkel[1], Jingrui Li[2], and Patrick Rinke[1,3] — [1]Department of Applied Physics, Aalto University, P.O.Box 11100, 00076 AALTO, Finland — [2]School of Electronic Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China — [3]Technical University of Munich, 85748 Garching, Germany

Perovskite-inspired quaternary mixed-metal chalcohalides (MMCHs, $\mathrm{M(II)_2M(III)Ch_2X_3}$) are an emerging materials class for photovoltaic's [1], that could overcome the stability and toxicity problems of halid perovskites [2], and still deliver high conversion efficiencies [3]. Compositional engineering enables the optimization of MMCH materials properties en route to commercialization.

We study the stability of MMCH alloys for three different compositional positions: the M(III), the Ch and the X site. We use a combination of density functional theory and machine learning to explore the compositional space of the alloys [4] and to compute their convex hulls. For x site alloying, for example $[\mathrm{Sn_2InS_2(Br_{1-c}I_c)_3}]$, we obtained stable structures for $c = \frac{1}{3}$ and $c = \frac{2}{3}$ for the $Cmcm$ phase and for $c = \frac{1}{6}$ and $c = \frac{1}{3}$ for the $Cmc2_1$ phase, but not for $P2_1/c$. The energetically favored structures (at $c = \frac{1}{3}$) are highly symmetrical and exhibit a layered pattern. Every third halogen layer is fully occupied by iodine whereas the other two layers are filled with bromine.

[1] *Chem. Mater.* **35**, 7761-7769 (2023), [2] *Z. Anorg. Allg. Chem.* **468**, 91-98 (1980), [3] *Mater. Horiz.* **8**, 2709 (2021). [4] *Phys. Rev. Materials* **6**, 113801 (2024).

HL 1.3 Mon 10:00 H13

Versatile Two-Step Process for Enhanced Stability and Efficiency in Perovskite Top Cells for Tandem Photovoltaics — •Ronja Pappenberger[1,2], Roja Singh[1,2], Alexander Diercks[2], and Ulrich W. Paetzold[1,2] — [1]Institute of Microstructure Technology, KIT, Germany — [2]Light Technology Institute, KIT, Germany

To achieve highly efficient 2T perovskite/silicon (Si) tandem solar cells (TSCs), textured-front Si bottom cells provide superior light-harvesting capabilities, making higher short-circuit current densities of TSC possible. A promising approach to fabricating uniform, high-quality perovskite films on these textured Si cells is the solution-based two-step method. One of the main challenges for perovskite solar cells (PSCs) remains their long-term stability. While methylammonium (MA)-based PSCs have demonstrated some of the highest efficiencies, their instability continues to pose a major obstacle. In this work, a versatile two-step process is employed – replacing MA with formamidinium – which maintains high efficiency, improves open-circuit voltage and enhances stability. A further performance boost is achieved by implementing a dual passivation strategy using $\mathrm{PDAI_2}$ and BAI for bulk and surface passivation. This leads to a stable power output exceeding 20.8% for $E_\mathrm{g} = 1.67$ eV due to reduced non-radiative recombination at the perovskite/ETL interface and improved film crystallization, enhancing charge carrier extraction. The long-term stability is also distinctly improved. When implemented on textured Si bottom cells, this process delivers efficiencies exceeding 24% for lab-scale monolithic perovskite/Si TSCs with a 1 $\mathrm{cm^2}$ active area.

HL 1.4 Mon 10:15 H13

Recombination at grain boundaries in Cd(Te,Se) thin films in comparison with other photovoltaic absorber layers — •Luka Blazevic[1], Sebastian Weitz[1], Elisa Artegiani[2], Alessandro Romeo[2], and Daniel Abou-Ras[1] — [1]Helmholtz-Zentrum Berlin, Germany — [2]Universita di Verona, Italy

The role of grain boundaries on the device performance is of concern for all polycrystalline absorbers in photovoltaic solar cells. In the present work, recombination velocities s_{GB} at grain boundaries in Cd(Te,Se) thin-film absorbers were determined from cathodoluminescence (CL) intensity distributions, which were acquired together with electron backscatter diffraction (EBSD) and energy-dispersive X-ray spectroscopy (EDXS) maps. The resulting s_{GB} values exhibited ranges over several orders of magnitude ($10^1 - 10^3$ cm/s). These wide value ranges are in good agreement with those obtained on other photovoltaic absorber materials (multicrystalline Si, $\mathrm{Cu(In,Ga)Se_2}$, $\mathrm{Cu_2ZnSn(S,Se)_4}$). The present work suggests a model comprising the enhanced, nonradiative Shockley-Read-Hall recombination at grain boundaries as well as the upward/downward band bending (± several 10 meV) at these planar defects. This model can reproduce successfully the experimental s_{GB} values from various photovoltaic absorber materials and provides also ranges for the effective defect densities as well as their capture cross-sections at the grain boundaries. It will be shown that typical losses in the open-circuit voltage of the corresponding solar cells due to grain-boundary recombination in the absorbers are few 10 mV.

HL 1.5 Mon 10:30 H13

Microscopic origins of band-gap broadening and its relationship with Urbach tails in photovoltaic absorbers — •Daniel Abou-Ras — Helmholtz-Zentrum Berlin, Germany

The broadening of absorption edges is a general feature found in numerous semiconductors used as absorber layers for thin-film solar cells. Since this broadening gives rise to radiative losses of the open-circuit voltage, it is of importance to control the broadening by corresponding material design of the photovoltaic absorber materials. The present work provides an overview of the microscopic origins of band-gap broadening, addressing not only compositional aspects and microstrain, but also electrical and optoelectronic properties on the sub-μm scale. In addition, the Urbach energy extracted from absorptance or quantum efficiency spectra has been used broadly to quantify disorder in a material. However, up to date, it has not only not been clarified what the microscopic origins of Urbach tails are; the present contribution also shows that there is no direct correlation between the broadening of the absorption edge and the Urbach energy of a semiconductor, as verified for about 30 different photovoltaic absorbers.

HL 1.6 Mon 10:45 H13

Minimizing V_{OC} losses in high bandgap perovskite solar cells for the application in perovskite/perovskite/silicon triple-junction solar cells — •Athira Shaji[1,2], Minasadat Heydarian[1,3], Oliver Fischer[1,3], Michael Günthel[1], Orestis Karalis[4], Maryamsadat Heydarian[1], Alexander J. Bett[1], Hannes Hempel[4], Martin Bivour[1], Florian Schindler[1], Martin C. Schubert[1], Stefan W. Glunz[1,3], Andreas W. Bett[1,2], Juliane Borchert[1,3], and Patricia S. C. Schulze[1] — [1]Fraunhofer Institute for Solar Energy Systems ISE, Germany — [2]University Freiburg, Institute of Physics, Germany — [3]University of Freiburg, Department of Sustainable Systems Engineering, Germany — [4]Helmholtz-Zentrum Berlin, Solar Energy Division, Germany

The high bandgap (HBG) top cell is the main source of V_{OC} loss in perovskite/perovskite/silicon triple junction solar cells due to photoinduced phase segregation, non-radiative recombination at the perovskite bulk and interface with the charge transport layers (CTLs), as well as energetic misalignment between the perovskite layer and the CTLs. The starting point of this work was a triple-cation double-halide perovskite composition with a bandgap of 1.83 eV. By implementing a multi-faceted optimization approach, an average improvement in V_{OC} of 250 mV was achieved for HBG perovskite solar cells. Replacing the reference HBG perovskite with the optimised top cell in perovskite/perovskite/silicon triple-junction solar cells results in the improvement of V_{OC} by 124 mV, and the champion device achieves a voltage above 3 V.

15 min. break

HL 1.7 Mon 11:15 H13

The Effect of Overdamped Phonons on the Fundamental Band Gap of Perovskites — •Xiangzhou Zhu and David A. Egger — Physics Department, TUM School of Natural Sciences, Technical University of Munich, 85748 Garching, Germany

Different from conventional semiconductors, halide perovskites (HaPs) exhibit unique anharmonic fluctuations that strongly influence optoelectronic properties. Recent studies have shown that in specific temperature regimes, the strong phonon-phonon interactions in HaPs lead to overdamped phonons, where vibrational lifetimes drop below one oscillation period. However, the relationship between these overdamped phonons and atomic fluctuations, as well as their impact on optoelectronic properties, are not fully understood. Here, using molecular dynamics (MD) simulations and augmented stochastic Monte Carlo methods that account for phonon renormalization and imaginary modes, we contrast the band gap behavior of two anharmonic perovskite materials, $SrTiO_3$ and $CsPbBr_3$, of which only the latter exhibits overdamped phonons.[1] Our results show that the overdamped phonon dynamics in $CsPbBr_3$ drive slow atomic fluctuations that are not adequately captured by conventional phonon quasiparticle descriptions. Importantly, we show that these overdamped phonon lead to significant renormalization of the band gap. Our work disentangles the consequences of anharmonic effects on the optoelectronic properties and electron-phonon interactions in perovskites.

[1] Zhu, X. & Egger, D. A. arXiv:2406.05201 (2024).

HL 1.8 Mon 11:30 H13

Polymorphism at surface in $CsPbI_3$ from first principles — •Jasurbek Gulomov[1], Guido Roma[1], Jacky Even[2], and Marios Zacharias[2] — [1]Université Paris-Saclay, CEA, Service de recherche en Corrosion et Comportement des Matériaux, SRMP, Gif sur Yvette, 91191, France — [2]Université Rennes, INSA Rennes, CNRS, Institut FOTON - UMR 6082, F-35000 Rennes, France

Halide perovskites show great potential for optoelectronics and photovoltaics, but challenges with ion migration and phase stability remain.Atomic-scale phenomena at surfaces and interfaces must be understood to block ion migration and enhance passivation. A peculiar property of these materials is the tendency to gain energy by disordered structural distortions, dubbed polymorphism, in contrast to the view of a perfectly symmetric monomorphous structure. Using first-principles calculations, we investigate the electronic and structural properties of polymorphous bulk $CsPbI_3$ and its 100 surface with two terminations. For the bulk, we generate a dynamically stable polymorphous structure for the cubic high-temperature phase using the method recently proposed by M. Zacharias et al. [1]. The energy gain and band gap opening are essentially linked to the increased average length of Pb-I bonds. Then we extend the concept of polymorphism to the surface, analyzing surface dipoles and work functions by comparing monomorphous and polymorphous slabs with experimental data. Our results tend to confirm the occurrence of polymorphism at surfaces in $CsPbI_3$.

[1] Zacharias, M., et al., npj Comput. Mater. 9, 153 (2023).

HL 1.9 Mon 11:45 H13

Benchmarking approximations for the theoretical prediction of positron lifetimes in halide perovskites — Kajal Madaan[1], •Guido Roma[1], Jasurbek Gulomov[1], Pascal Pochet[2], Catherine Corbel[3], and Ilja Makkonen[4] — [1]Université Paris-Saclay, CEA, Service de recherches en Corrosion et Comportement des Matériaux, SRMP, 91191 Gif sur Yvette, France — [2]Department of Physics, IriG, Univ. Grenoble-Alpes and CEA, Grenoble, France — [3]LSI, CEA/DRF/IRAMIS, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, 91120, France — [4]Department of Physics, University of Helsinki, P.O. Box 43, FI-00014 Helsinki, Finland

Positron annihilation spectroscopy is a well recognized tool for probing vacancies in materials. Recent applications of this technique to $APbX_3$ halide perovskites are sparse, and the rare theoretical predictions of positron lifetimes in these materials, published in association with experiments, do not fully agree with each other. These works suggest that vacancies on the A site are not detected. In our theoretical study we thoroughly revisit and compare several approximations for the electron-positron correlation functional, applied to methylammonium lead iodide ($MAPbI_3$) and $CsPbI_3$ and their vacancies. The discrepancies between the approaches make it difficult to unequivocally exclude the presence of methylammonium vacancies in $MAPbI_3$. Moreover, when using a truly nonlocal electron-positron correlation functional, the predicted positron density in a vacancy presents peculiar features and a much lower binding energy to the vacancy with respect to semilocal approximations.

HL 1.10 Mon 12:00 H13

Dynamics of electronic surface states in halide perovskites using machine-learning force fields — •Frederico Delgado[1], Frederico Simões[1], Waldemar Kaiser[1], Leeor Kronik[2], and David A. Egger[1] — [1]Physics Department, TUM School of Natural Sciences, Technical University of Munich, Germany — [2]Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Israel

The photovoltaic performance exhibited by bulk halide perovskites (HaPs) hinges on their excellent optoelectronic properties, which have been extensively investigated. Nonetheless, extended defects like surfaces are ubiquitous, and as such, their impact on such properties requires further, careful investigation. Rigorous examination of dynamics in this context through ab-initio molecular dynamics implies large computational costs, which are here circumvented by the use of machine learning (ML) force fields. In this study, we demonstrate the transient and shallow nature of surface states in $CsPbBr_3$. We shed light on the mechanisms which underpin the behaviour of such states through the framework of local, internal dipoles. Our results aid in rationalizing the benign nature of surfaces in $CsPbBr_3$, and further the understanding of the correlation between structural dynamics and optoelectronic properties of HaP surfaces.

HL 1.11 Mon 12:15 H13

Comprehensive High-Throughput DFT Study of Intrinsic Defects and Dopability in p-type Zn3P2 for Photovoltaic Applications — •Nico Kawashima[1,2,3] and Silvana Botti[1,3] — [1]Ruhr-Universität, Bochum, Germany — [2]Friedrich-Schiller-Universität, Jena, Germany — [3]RC FEMS, Bochum, Germany

Zn_3P_2 has attracted significant interest as a thin-film absorber material for photovoltaic applications due to its intrinsic p-type conductivity and earth-abundant constituents. However, the nature of the dominant native defects – whether phosphorus interstitials (P_{i}) or zinc vacancies (V_{Zn}) – remains a subject of debate, with implications for the material's electronic structure and dopability through mechanisms such as Fermi-level pinning and defect compensation.

We perform a high-throughput density functional theory (DFT) analysis to systematically investigate both intrinsic point defects and potential extrinsic dopants. By resolving the ground-state configurations and formation energies of key native defects, we provide a clearer understanding of their impact on the electronic landscape. This insight is then applied to evaluate a range of extrinsic dopants, predicting their incorporation and activation potentials in the presence of native defects.

Our study offers a comprehensive framework that links intrinsic defect behavior with extrinsic doping strategies, providing critical guidance for tuning the electrical properties of Zn_3P_2. The findings present experimentally actionable insights that can drive the optimization of Zn_3P_2 for next-generation photovoltaic devices.

HL 1.12 Mon 12:30 H13

Density functional theory study of hydrogen passivation mechanisms in defective silicon — •Hania Azzam[1], Tobias Binninger[1], and Michael Eikerling[1,2] — [1]Theory and Computation of Energy Materials (IET-3), Institute of Energy Technologies, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — [2]Chair of Theory and Computation of Energy Materials, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany

Silicon heterojunction (SHJ) solar cells offer high-effeciency energy conversion, with reported efficiencies up to 27%. Their performance and durability depend on effective passivation of dangling bonds at the amorphous/crystalline silicon interface, where electron-hole recombination reduces efficiency. Hydrogen atoms play a crucial role in passivating those dangling bonds, minimizing recombination loses. Recent experimental studies by IMD-3 at Forschugnszentrum Jülich showed performance improvements after light soaking, a process where solar cells are exposed to intensive light at elevated temperatures. It is hypothesized that light soaking activates hydrogen migration toward defect sites. This theoretical study explores hydrogen passivation mechanisms in defective silicon for SHJ solar cells. Using Density Functional Theory (DFT), we analyze how silicon vacancies alter the electronic structure of Si-H systems, introducing localized defect states within the band gap and shifts in Fermi level, and subsequently investigate the changes induced by hydrogen passivation. These insights contribute to understanding the beneficial effects of light soaking on SHJ solar cells.

HL 1.13 Mon 12:45 H13

First principles theory of nonlinear long-range electron-phonon interaction — •Matthew Houtput[1,2], Luigi Ranalli[2], Jacques Tempere[1], and Cesare Franchini[2] — [1]University of Antwerp, Belgium — [2]University of Vienna, Austria

Electron-phonon interactions in a solid are crucial for understanding many interesting material properties, such as transport properties and the temperature dependence of the electronic band gap. For harmonic materials, the linear interaction process where one electron interacts with one phonon is sufficient to quantitatively describe these properties. However, this is no longer true in anharmonic materials with significant electron-phonon interaction, such as quantum paraelectrics and halide perovskites. Currently, the only available models for nonlinear electron-phonon interaction are model Hamiltonians, written in terms of phenomenological parameters. Here, we provide a microscopic semi-analytical expression for the long-range part of the 1-electron-2-phonon matrix element, which can be interfaced with first principles techniques. We show that unlike for the long-range 1-electron-1-phonon interaction, the continuum approximation is not sufficient and that the entire phonon dispersion must be taken into account. We calculate an expression for the quasiparticle energies and show that they can be written in terms of a 1-electron-2-phonon spectral function. To demonstrate the method in practice, we calculate the 1-electron-2-phonon spectral function for $KTaO_3$ from first principles. The framework in this article bridges the gap between model Hamiltonians and first-principles calculations for the 1-electron-2-phonon interaction.