

KFM 20: Perovskite and Photovoltaics 2 (joint session HL/ CPP/KFM)

Time: Wednesday 15:00–18:15

Location: H34

KFM 20.1 Wed 15:00 H34

Electronic structure analysis of the interface of a TiO₂ electron-transport layer with a perovskite CsPbI₃ photovoltaic absorption layer — ●AMIRHOSSEIN BAYANI¹, JULIAN GEBHARDT¹, and CHRISTIAN ELSÄSSER^{1,2} — ¹Fraunhofer Institute for Mechanics of Materials IWM, Wöhlerstrasse 11, 79108 Freiburg, Germany — ²Freiburg Materials Research Center (FMF), Albert-Ludwigs-University Freiburg, 79104 Freiburg, Germany

Lead-based hybrid perovskite halides are currently the most promising light absorbing materials to supplement or even replace Si in next generation solar cells. With intensive research of the bulk material properties in recent years, a strong interest emerges in studying the interfaces to the contact layers in order to reach the final boost of solar efficiency in devices. Here, we study the interface of CsPbI₃ with TiO₂ as model interface for a perovskite with an electron transport layer. In particular, we investigate the rutile-TiO₂(001)[001] / CsPbI₃(001)[100] interface using self-energy corrected density functional theory. By this state-of-the-art modeling technique, we analyze the alignment of work-functions and investigate the band alignment at the interface.

KFM 20.2 Wed 15:15 H34

Influence of the Ionic Liquid BMIMBF₄ on the film formation and optoelectronic properties of MAPbI₃ — ●SIMON BIBERGER, KONSTANTIN SCHÖTZ, PHILIPP RAMMING, NICO LEUPOLD, RALF MOOS, ANNA KÖHLER, HELEN GRÜNINGER, and FABIAN PANZER — University of Bayreuth, Bayreuth, Germany

Today, metal halide perovskite solar cells (PSCs) are one of the most promising emerging photovoltaic technologies. However, their still limited stability is a main hurdle for their successful commercialization. In the past, various approaches have been developed to improve the long-term stability and performance of PSCs. Here ionic liquids (IL) as additives have attracted much attention as they passivate defects and suppress ion migration. In this work, we investigate the effect of the IL BMIMBF₄ on the film formation and optoelectronic properties of the model halide perovskite MAPbI₃. By multimodal in situ optical spectroscopy, we investigate the formation of the perovskite film during solution processing via one-step spin coating and a solvent engineering approach and how the film formation alters when the IL is added to the precursor solution. We find that the IL does not impact the formation of perovskite-solvent complexes, but the perovskite growth rate decreases with increasing IL content in the precursor solution. Additionally, we reveal that the IL already interacts with precursor materials and changes the evolution of the PbI₄²⁻ properties. Thus, our work provides important insights into how decisive ILs impact the sensitive interconnection between precursor properties, film formation process and final optoelectronic functionality of perovskite thin films.

KFM 20.3 Wed 15:30 H34

Transversal halide motion enables sharp optical absorption profiles in halide perovskites — ●SEBASTIÁN CAICEDO-DÁVILA, CHRISTIAN GEHRMANN, XIANGZHOU ZHU, and DAVID A. EGGER — Department of Physics, Technical University of Munich, Garching, Germany

Despite their strong vibrational anharmonicity, halide perovskites (HaPs) exhibit favorable optoelectronic properties, which facilitate their outstanding performance in solar cells, comparable to high-quality inorganic semiconductors. In this contribution, we explore the mechanisms and consequences of dynamic structural flexibility in CsPbBr₃ using first-principles molecular dynamics based on density-functional theory. We show that large Br displacements occur on planes that are transversal to the Pb-Br-Pb bonding axis. This *transversality* is concurrent with vibrational anharmonicity, results in short-ranged disorder correlations, and sharpens the joint-density of states rise at finite temperature. Finally, we contrast these results to the case of PbTe, which shares key properties with CsPbBr₃ but cannot exhibit any *transversality*, to show that this system features wider band-edge distributions and longer-ranged disorder correlations. These findings are relevant for connecting the structural flexibility and bonding of the halide perovskite structure with the sharp optical absorption of these materials.

KFM 20.4 Wed 15:45 H34

Investigating underlying mechanisms of K doping on stability of single- and mixed-cation perovskite solar cells with experimental and computational informed modelling — SAIED MOLLAVALI, MOHAMMAD MOADDELI, and ●MANSOUR KANANI — Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran

Recent studies revealed that the interstitial occupancy of potassium in single/mixed-cation based perovskite structures could hinder the ion migration mechanisms near interfaces, and therefore leads to a better structural stability. However, the underlying stability enhancement mechanisms and probable side effects of additional K atoms in cooperate with other organic/inorganic constituents, with a long-range electronic bonding character, is not clear completely. In this study, the effect of doping K on the structural, morphological, electronic, and optical properties of different perovskite structures is investigated experimentally and computationally. The beneficial effect of interstitial K atom on long-range bonding of I atoms with organic molecules is observed. Furthermore, no degradation from additional K is detected for specific range of doping. This result opens a new insight on constructive impact of inorganic dopant on stability issue in perovskite solar cells. SEM, XRD, Photoluminescence and optical absorbance analysis were performed on the perovskite layer. The one layer-based experimental data incorporation with DFT based results were informed into the SCAPS-1D solar cell simulator package to predict cell efficiency, systematically.

KFM 20.5 Wed 16:00 H34

Revealing efficiency losses due to mobile ions in perovskite solar cells — ●SAHIL SHAH, JARLA THIESBRUMMEL, and JONAS DIEKMANN — University of Potsdam, Germany

Perovskite semiconductors are distinct from most other semiconductors due to a large number of mobile ions in the active layer (e.g., iodide and methylammonium ions and vacancies, and others). Thus, ion dynamics have a critical impact on the performance and stability of perovskite-based applications.

In this work, we will show how the ionic density and induced losses change with device degradation under elevated temperatures and continuous light illumination. This is investigated via a simple and newly developed method *fast-hysteresis* which is a JV scan at a faster rate (~1000 Vs-1) which prevents the perturbation of mobile ions and we get the true ion free potential of the device. The fast-hysteresis measurements are corroborated by transient charge extraction and capacitance measurements as well as numerical simulations, which provide important insights into the dynamics of free electronic charges and mobile ions. We will then demonstrate how the mobile ions affect a range of commonly used mixed cation metal halide perovskite compositions and how the ionic losses vary with the charge transport layer.

Overall, the proposed methods quantify the ion-induced field screening, shed light on the complex device degradation process and PCE losses allow for a better understanding of several key phenomena in perovskite solar cells, and open up a large range of future experiments.

KFM 20.6 Wed 16:15 H34

Dissecting Ultrafast Polarization Responses in Lead Halide Perovskites via the THz-induced Kerr Effect — ●MAXIMILIAN FRENZEL¹, MARIE CHERASSE^{1,2}, JOANNA URBAN¹, FEIFAN WANG³, BO XIANG³, LEONA NEST¹, LUCAS HUBER³, MARTIN WOLF¹, X.-Y. ZHU³, and SEBASTIAN F. MAEHRLEIN¹ — ¹Fritz Haber Institute of the Max Planck Society, Department of Physical Chemistry, Berlin, Germany — ²LSI, CEA/DRF/IRAMIS, CNRS, Ecole Polytechnique, Institut Polytechnique de Paris, Palaiseau, France — ³Columbia University, Department of Chemistry, New York City, USA

The microscopic origin of the surprising optoelectronic properties of lead halide perovskite (LHP) semiconductors is still under debate. One hypothesis is that the highly polar and anharmonic lattice of LHPs influences their optoelectronic properties through dynamic charge carrier screening. We therefore study the ultrafast polarization response of the hybrid LHP MAPbBr₃ when exposed to transient electric fields in the form of intense, single-cycle THz pulses. By probing the THz-induced Kerr effect (TKE), we observe strong THz polarizability and complex ultrafast polarization dynamics. We perform 4-wave-mixing simulations, which show that it is crucial to account for anisotropic

and dispersive light propagation for the correct interpretation of the measured TKE signals. Finally, we unveil a coherent phonon response in MAPbBr₃, which we assign to the inorganic cage and conclude to be the dominating polarizable mode in this material. This finding highlights the role of the inorganic lattice for dynamic carrier screening and the related mechanism of charge carrier protection.

30 min. break

KFM 20.7 Wed 17:00 H34

Calculating the temperature-dependent band gap of the halide perovskite CsPbBr₃ — ●STEFAN SEIDL, CHRISTIAN GEHRMANN, XIANGZHOU ZHU, SEBASTIAN CAICEDO DAVILA, and DAVID A. EGGER — Department of Physics, Technical University of Munich, Garching, Germany

Theoretical calculations based on density functional theory (DFT) can predict thermal effects in the electronic structure by considering important phenomena, such as thermal lattice expansion and electron-phonon coupling. The latter can be calculated using a Monte-Carlo (MC) sampling approach that is formally rooted within the harmonic approximation, which has recently been shown to yield accurate temperature-dependent band gaps for inorganic semiconductors [1]. A complementary approach to predict thermal effects in the electronic structure is first-principles molecular dynamics (MD), which can account for vibrational anharmonicity that is an important effect for certain technologically relevant materials. Here, we assess the temperature-dependent band gap of the halide perovskite CsPbBr₃ in the cubic and orthorhombic phases employing the two different methods, MC and MD, and compare our findings with experimental results. This includes a discussion about the role of anharmonicity and the contributions from spin-orbit coupling and thermal lattice expansion.

[1] F. Karsai et al, New J. Phys. 20, 123008 (2018)

KFM 20.8 Wed 17:15 H34

Electronic structure prediction of hybrid organic-inorganic metal halide perovskites using cost-effective DFT-1/2 method — MOHAMMAD MOADDELI und ●MANSOUR KANANI — Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran

Hybrid organic-inorganic metal halide perovskites (OIHPs) have attracted much attention in the last decade because of tunable photovoltaic performance and low fabrication cost. Regarding the tunable parameters for controlling the fundamental properties of OIHPs, recent computational and data-driven based approaches can accelerate new material prediction procedure significantly. Density functional theory (DFT) is considered as fundamental block of many multiscale, high-throughput and data-driven approaches typically. However, because of complexity of electronic orbital in OIHP as well as high sensitivity of regarding properties to atomistic configuration, employing conventional computational approaches faces many obstacles or needs very expensive corrections. Underestimation of routine functionals used in DFT calculations push people apply expensive approaches such as hybrid functionals and GW approximation. Here, DFT-1/2 method with a normal computational cost has been used for determining not only the band gap but also the true form of valence and conduction bands of OIHPs. The results showed that, the method could preserve the known Rashba band splitting in the conduction band of mixed-cation perovskites, which is the source of longer carrier lifetime behavior.

KFM 20.9 Wed 17:30 H34

Phonon Signatures for Polaron Formation in an Anharmonic Semiconductor — ●FEIFAN WANG^{1,2}, WEIBIN CHU³, JIN ZHAO³, and X.-Y. ZHU¹ — ¹Columbia University, New York, NY, 10027 USA — ²Dept. of Materials, ETH Zurich, Switzerland — ³University of Science and Technology of China, Hefei, Anhui 230026, China

Polaron formation, in which charge carriers are dressed by a cloud of lattice distortions, is partially responsible for the long carrier lifetimes and diffusion lengths in the lead halide perovskite (LHP), a

superior optoelectronic material. Considerations of ferroelectric-like phonon anharmonicities of this system lead to the recent proposal of ferroelectric large polarons, which attributes efficient charge-carrier screening to the extended ordering of dipoles associated with inversion-symmetry-breaking unit cells. Here, we study electron-phonon coupling in Bi₂O₂Se, a semiconductor which bears resemblance to LHPs in ionic bonding, band transport with long carrier diffusion lengths, and dynamical phonon disorder as revealed by low-frequency Raman spectroscopy. Using coherent phonon spectroscopy, we show the strong coupling of an anharmonic phonon mode to photo-excited charge carriers, while the Raman excitation of this mode is symmetry-forbidden in the ground-state. Density functional theory calculations verify that the phonon mode originates from the symmetry reduction after charge injection and indicate the local dipole ordering induced by photo-excited electrons. This study provides an initial attempt to generalize the proposed charge-carrier screening model to account for the outstanding optoelectronic properties of defect-tolerant semiconductors.

KFM 20.10 Wed 17:45 H34

Tuning Perovskite Crystallization in the Hybrid Route — ●MOHAMED MAHMOUD, PATRICIA SCHULZE, ANDREAS BETT, and OUSSAMA ER-RAJI — Fraunhofer ISE

In 2009, perovskite solar cells were discovered in the solid-state that can be used not only as a single junction absorber but also in tandem configuration thanks to their bandgap tunability. It is a combination of organic and inorganic lead halide materials and they have the advantage of a strong absorption edge, defect tolerance and potential cheap production due to easy production methods such as spin coating or slot-die coating as a highly scalable production method. In the industry, double-sided textured silicon (DSTS) is commonly produced to overcome the reflection losses at surfaces. Spin coating of perovskite on top of DSTS resulted in low conformality which resulted in shunts and non-working solar cells. To overcome this issue, the hybrid route was developed, in which inorganic materials are co-evaporated using the thermal vapour deposition technique and then organic materials are spin-coated. By doing that, the high conformality of the thin film on top of the c-Si is achieved. However, the resulting perovskite grain size is in the nanometer scale. To increase the grain size - which results in higher short circuit current, lower grain boundaries and thus a more stable device - thermodynamics of the crystallization process need to be studied. In this work, using the thermodynamics fundamentals of crystallization, we tune the grain size of perovskite deposited via the hybrid route. In addition, we study the consequences of different grain sizes on the efficiency of the solar cell and especially on the stability.

KFM 20.11 Wed 18:00 H34

Dynamic nuclear spin polarization in lead halide perovskites — ●NATALIA KOPTEVA¹, DENNIS KUDLACH¹, MAREK KARZEL¹, MLADEN KOTUR¹, DMITRI YAKOVLEV¹, OLEH HORDICHUK², OLGA NAZARENKO², DMITRY DIRIN², MAKSYM KOVALENKO^{2,3}, and MANFRED BAYER¹ — ¹Experimentelle Physik 2, TU Dortmund, 44221 Dortmund, Germany — ²Laboratory of Inorganic Chemistry Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland — ³Laboratory for Thin Films and Photovoltaics Empa-Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland

Lead halide perovskites are promising for applications in spintronics due to the nanosecond coherence time of the resident carriers [1]. The primary source of losing spin coherence is the interaction with the fluctuating nuclear spin environment [2]. Optically oriented carrier spins polarize nuclei, which create an Overhauser field. Due to the different strengths of the hyperfine interaction with the nuclear spins, the electron and hole experience different magnitude and directions of the Overhauser field. To study the degree of nuclear spin polarization and fluctuation, we investigate the interaction of resident and optically created carrier spins with nuclei using the Hanle effect in the tilted magnetic field in bulk formamidinium caesium lead iodine bromide.

[1] V. V. Belykh et al., Nat. Commun. 10, 673 (2019)

[2] I. A. Merkulov et al., Phys. Rev. B 65, 205309 (2002)