

## CPP 10: Focus Session: When theory meets experiment: Hybrid halide perovskites for applications beyond solar I (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%. We have observed - with notable exceptions - a widening gap between experimental and theoretical efforts in the literature on halide perovskites. Further, a large fraction of the literature focuses on properties relevant for optoelectronic applications, while we envision a much wider scope for these materials, e.g. in spintronic and electro-chemical applications. The purpose of this focus session is to provide a platform for theorists and experimentalists working in this field, to interact, present state-of-the-art methods, and exchange their ideas on future directions for this technologically relevant class of materials beyond the current focus on optoelectronics.

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

Time: Monday 9:30–12:00

Location: POT 251

**Invited Talk** CPP 10.1 Mon 9:30 POT 251  
**Anharmonic semiconductors - Lessons Learned from Halide perovskites** — ●OMER YAFFE — Weizmann Institute of Science, Rehovot, Israel

In semiconductor physics, the dielectric response, charge carrier mobility and other electronic material properties at finite temperatures, are always treated within the framework of the harmonic approximation. This approach is very successful in capturing the properties of tetrahedrally bonded semiconductors such as silicon and GaAs.

In my talk, I will show that 2D and 3D halide perovskites are fundamentally different due to their strongly anharmonic lattice dynamics. Large amplitude, local polar fluctuations induced by lattice anharmonicity localize the electronic states and enhance the screening of electric charge within the material. In other words, in some aspects, halide perovskites behave more like a liquid than a crystalline solid. I will also discuss the implications of these findings on other families of semiconductors such as organic and rock-salt semiconductors.

**Invited Talk** CPP 10.2 Mon 10:00 POT 251  
**Lattice Screening of Excitons in Lead Halide Perovskites from First Principles** — ●MARINA R. FILIP<sup>1</sup>, JONAH B. HABER<sup>2</sup>, and JEFFREY B. NEATON<sup>2,3,4</sup> — <sup>1</sup>Department of Physics, University of Oxford — <sup>2</sup>Department of Physics, UC Berkeley — <sup>3</sup>Molecular Foundry and Materials Science Division, Lawrence Berkeley National Laboratory — <sup>4</sup>Kavli Energy NanoSciences Institute at Berkeley

Dielectric screening in semiconducting and insulating crystals generally originates both from electrons and polar phonons. Since photoexcited electron-hole pairs interact within this dielectric environment, both the electronic and lattice components of the screening can have important contributions to excitonic properties; for lead-halide perovskites, this is suggested from both theoretical and experimental evidence [1,2]. However, standard *ab initio* GW-BSE methodology for calculating optical excitations does not capture dynamic lattice polarization effects. In this talk I will present our extension of the GW-BSE method, to include lattice contributions to the screening. I will show that in heteropolar semiconductors with weakly bound excitons, dynamic lattice polarization can significantly reduce the exciton binding energy, and I will demonstrate this effect for the CsPbX<sub>3</sub> (X = Cl, Br, I) perovskites. Furthermore, I will discuss more generally the lattice contribution to the exciton binding energy in heteropolar semiconductors, as it emerges from a generalization of the Wannier-Mott model to include dynamical lattice polarization effects. [1] Miyata et al, Nat. Phys. 11, 582 (2015) [2] Umari et al, JPCL, 9, 3, 620 (2018). Work supported by the US DoE in the C2SEPEM center; computational resources from NERSC.

15 min. break.

**Invited Talk** CPP 10.3 Mon 10:45 POT 251  
**Structural dynamics and disorder in halide perovskites** — ●DAVID EGGER — Department of Physics, Technical University of Munich, 85748, Garching, Germany

Halide perovskites (HaPs) are highly promising materials for several optoelectronic applications. HaPs are also very interesting scientifically because of the peculiar structural dynamics that occur in the material. These include the appearance of massive structural disorder and anharmonic effects already at room temperature, which challenge our current understanding of coupling between lattice vibrations and optoelectronic properties in a semiconductor.

In this talk, I will present our recent explorations of the consequences of the unusual structural phenomena in HaPs for their optoelectronic properties. Theoretical calculations based on density functional theory, molecular dynamics, and tight-binding modeling will be used to examine the impact of structural dynamics on pertinent device-relevant observables. Consequences of the structural dynamics and anharmonicity in HaPs will be discussed for the charge-carrier mobility, Urbach energy, and defect energetics. It will be shown that the impact of the unusual structural dynamics on the optoelectronic properties of HaPs cannot be neglected when understanding these materials microscopically and designing new functional compounds.

CPP 10.4 Mon 11:15 POT 251  
**Optoelectronic properties of lead-free double-perovskites from first principles** — ●RAISA I. BIEGA<sup>1</sup>, MARINA R. FILIP<sup>2,3</sup>, LINN LEPPERT<sup>1</sup>, and JEFFREY B. NEATON<sup>2,3,4</sup> — <sup>1</sup>Institute of Physics, University of Bayreuth, Bayreuth, Germany — <sup>2</sup>Department of Physics, University of California, Berkeley, USA — <sup>3</sup>Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, USA — <sup>4</sup>Kavli Energy NanoSciences Institute, Berkeley, USA

Power conversion efficiencies of single junction solar cells with lead-based halide perovskite absorbers have exceeded 25%. However, stability concerns have stimulated efforts for finding substitutes with similar optoelectronic properties, i.e., small band gaps, low effective masses and small exciton binding energies. Double perovskites containing alternating mono- and trivalent metal cations have emerged as one such alternative. Here we present first principles calculations of the electronic structure and excited states of the double perovskites Cs<sub>2</sub>AgBX<sub>6</sub> (B=Bi, Sb and X=Br, Cl). We use density functional theory and *ab initio* Green's function-based many-body perturbation theory within the GW and Bethe-Salpeter equation approach to calculate band structures and absorption spectra of these materials. Our results provide insights into the nature of optical excitations and suitability for photovoltaic and other light harvesting applications.

We acknowledge computational resources provided by NERSC, a DOE Office of Science User Facility supported by the U.S. Department of Energy and financial support by the DFG Programs SFB840 and GRK1640.

CPP 10.5 Mon 11:30 POT 251  
**First principles calculations for blue-emitting organic-inorganic halide perovskites** — ●IVOR LONCARIC<sup>1</sup>, LUCA GRISANTI<sup>1</sup>, JASMINKA POPOVIC<sup>1</sup>, and ALEKSANDRA DJURISIC<sup>2</sup> — <sup>1</sup>Rudjer Boskovic Institute, Zagreb, Croatia — <sup>2</sup>The University of Hong Kong

Ruddlesden-Popper halide perovskite (RPP) materials are of significant interest for light-emitting devices since their emission wavelength can be controlled by tuning the number of inorganic layers *n*. However, RPP films typically contain phases with different *n* which hinders the achievement of pure blue emission from *n*=2 films. Furthermore, energy funneling phenomenon, which involves energy transfer from lower *n* (higher energy) to higher *n* (lower energy) domains resulting in a brighter, but red-shifted emission, represents the further difficulty in obtaining pure blue emission from *n*=2 RPP emitters. By performing DFT calculations at room temperature we obtained an improved understanding of the effect of spacer cation on RPP properties. The calculations can be compared to real experimental conditions and give an insight into the feasibility of the stabilization of *n*=2 perovskite phase.

CPP 10.6 Mon 11:45 POT 251

**Computing temperature-dependent band gap distributions of halide perovskites with a first-principles tight-binding approach** —**•**MAXIMILIAN J. SCHILCHER<sup>1</sup>, MATTHEW Z. MAYERS<sup>2</sup>, LIANG Z. TAN<sup>3</sup>, DAVID R. REICHMAN<sup>2</sup>, and DAVID A. EGGER<sup>1</sup> — <sup>1</sup>Department of Physics, Technical University of Munich, 85748 Garching, Germany — <sup>2</sup>Department of Chemistry, Columbia University, New York, NY 10027, USA — <sup>3</sup>Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Due to their remarkably soft lattice and large temperature-induced nuclear fluctuations, it is challenging to understand the microscopic origin of the fascinating optoelectronic properties of halide perovskites (HaPs). In order to reveal their electronic and optical characteristics,

one can apply well-established theoretical methods, such as density functional theory (DFT). However, conventional DFT calculations are limited in addressing the impact of complex structural effects in HaPs that require the simulation of large supercell sizes and nuclear dynamical phenomena.

In this work, we employ a recently developed tight-binding (TB) approach [1], which is parametrized on the basis of DFT calculations, and apply it to trajectories obtained from efficient molecular dynamics calculations at various temperatures. We compute dynamic band-gap distributions for several HaPs to estimate the influence of temperature on these distributions, in order to explain the electronic and optical characteristics of HaPs around room temperature.

[1] M. Z. Mayers, et al., *Nano Lett.* 18, 8041-8046 (2018).