Unsolved Mysteries of Halide Perovskites Aron Walsh; Imperial College London, London, United Kingdom.

Perovskites are the wonder compounds of materials science, with examples of dielectrics, semiconductors, metals, and superconductors. This talk will address the chemical and physical properties that make halide perovskites unique. Following six years of intensive research, there has been a number of breakthroughs in understanding, but many challenges and opportunities remain.

These organic-inorganic semiconductors satisfy the optoelectronic criteria for an active photovoltaic layer, i.e. spectral response in the visible range combined with light electron and hole effective masses. In addition, they are structurally and compositionally flexible with large dielectric constants, and the ability to alloy on each of the lattice sites. To understand the success of methylammonium lead iodide photovoltaics, we have been applying materials theory and simulation across multiple length scales [1-5].

I will discuss issues ranging from disorder associated with molecular rotations and tilting of the inorganic network, to macroscopic polarisation arising from charged defect formation and diffusion. A number of unsolved mysteries will be outlined including self-healing effects, apparent ferroelectricity, light-enhanced ion transport, and ultimately, the origin of their high performance in optoelectronic devices.

This research has been supported by the Royal Society and a wide collaboration network with contributions from current and former group members including Federico Brivio, Keith Butler, Jarvist Frost, Jonathan Skelton, Katrine Svane, Ruoxi Yang, Lucy Whalley, Youngkwang Jung, Jacob Wilson, and Samantha Hood.

natural multiple quantum wells (QWs) with the semiconducting perovskite layers representing the wells and the insulating organic spacers representing the barriers. The width of the barrier is fixed and depends only on the length of the A’ cation, while the width of the well can be adjusted by varying the thickness of perovskite slabs, which is defined by the n variable in \((A')_{2}(A)_{n-1}MnX_{3n+1}\). It is critical to understand the thermodynamic and chemical limitations of the maximum layer thickness that can be sandwiched between the organic bilayers while retaining the structural integrity of the 2D perovskite. The so-called “hollow” perovskites are a new form which lies between the conventional 3D and 2D perovskites. While the overall network is 3D there massive vacancies in it that give the materials different properties. The chemical and structural aspects of these materials will be presented and devices made from them will be described.

9:30 AM *ET05.01.03
Halide Perovskites—One of a Kind or Harbinger of Novel Optoelectronic Materials
David Cahen1, 2; 1Weizmann Institute of Science, Rehovot, Israel; 2Bar Ilan University, Centre for Nanotechnology and Advanced Materials, Ramat Gan, Israel.

Halide Perovskites, HaPs, may be mostly normal (inorganic) semiconductors and, indeed, we should be careful to describe them with concepts from organic electronics. HOWEVER, it is remarkable that a material with over-all high quality optoelectronic properties can result from fast, low temperature, solution preparation. This suggests that there may also be issues with using some concepts from “classical” semiconductors. Now we can ask if minor revisions will do or if major ones are needed (rejection is not an option; HaPs exist…).

For that we need to define and understand what remains special about HaPs and what is/are the reason(s) for what, if anything, remains special. Being able to do so may help answer the nagging question if this is all because Pb is so unique, or if we can generalize to find other materials like these. I will consider the general question and, as things look now, 5.5 months before the talk, consider the relevance of mechanical, in conjunction with other properties, to challenge what we think we know about defects in HaPs, note a confusing semantic issue and more, to arrive at an answer, to guide us in future work.

Work done with Gary Hodes (Weizmann), with input from many others, whom I will credit in my talk.

10:00 AM BREAK

10:30 AM *ET05.01.04
Theory and Modeling of Correlated Ionic and Electronic Motions in Hybrid Organic-Inorganic Perovskites
Matthew Mayers1, 2, Liang Z. Tan1, David A. Egger4, Andrew M. Rappe1 and David Reichman1; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Chemistry, Columbia University, New York, New York, United States; 4University of Regensburg, Regensburg, Germany.

The perovskite crystal structure hosts a wealth of intriguing properties, and the renaissance of interest in halide (and hybrid organic-inorganic) perovskites (HOIPs) has further broadened the palette of exciting physical phenomena. Breakthroughs in HOIP synthesis, characterization, and solar cell design have led to remarkable increases in reported photovoltaic efficiency.

However, the observed long carrier lifetime and PV performance have eluded comprehensive physical justification. The hybrid perovskites serve as an enigmatic crossroads of physics. Concepts from crystalline band theory, molecular physics, liquids, and phase transition models have been applied with some success, but the observations of HOIPs make it clear that none of these conceptual frameworks completely fits. In this talk, recent theoretical progress in understanding HOIPs will be reviewed and integrated with experimental findings. The large amplitude motions of HOIPs will be highlighted, including ionic diffusion, anharmonic phonons, and dynamic incipient order on various length and time scales. The intricate relationships between correlated structural fluctuations, polar order, and excited charge carrier dynamics will also be discussed.

11:00 AM ET05.01.05
Low Charge Mobility in SOFT Polar Crystals is Fundamental! The Case of Halide Perovskites
Yevgeny Rakita, Gary Hodes and David Cahen; Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel.

The combination of properties halide perovskites (HaPs) possesses (e.g., high absorption coefficient, low effective mass, low exciton binding energy, low carrier recombination lifetimes, etc.) should (and does) allow high-performing optoelectronic devices. However, there is one fundamental property that does not fit the expected prognosis coming from the superior material’s properties – its carrier mobility. When comparing mobility values of HaPs (~1-100 cm²/Vs) with those of polar semiconductors, such as GaAs or CdTe (~10⁻⁴-10⁻¹ cm²/Vs), a significant difference is revealed. Mobility temperature dependence, which points on the scattering mechanism, is found in HaPs, GaAs, CdTe and other polar semiconductors to be similar and suggest scattering by polar optical phonon. Low defect density, as found for HaPs (~10¹⁰ cm⁻³ in single crystals) as well as for other high-quality polar semiconductors (e.g., GaAs and CdTe), make scattering by defects insignificant (at temperatures > ~100 K). Therefore, the origin of charge scattering and, thus, their mobility, probably relate to more intrinsic properties of these polar semiconductors.

So what makes the mobility in HaPs to be so different from that in other polar semiconductors? Correlation of experimentally-derived physical values from semiconductors, including HaPs, reveals a clear correlation between the mechanical properties (or what is called a ‘deformation potential’) and the charge mobility. In fact, the softer the material, the lower its mobility. In my talk, I will explain the origins for such relation, which suggest that in a soft material such as HaPs mobility will never reach values as high as in GaAs.


11:15 AM ET05.01.06
The Polar Liquid Sublattice in Single Crystal Perovskite CH₃NH₃PbBr₃(001)
Prescott E. Evans1, Marin Pink2, Ayan Zhumekenov3, Guanhua Hao1, Yaroslav Lozovyy2, Osman M. Bakr1, Peter Dowben1 and Andrew J. Yost1; 1University of Nebraska-Lincoln, Lincoln, Nebraska, United States; 2Indiana University, Bloomington, Indiana, United States; 3King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The dynamic motion, within the lattice of a single crystal CH₃NH₃PbBr₃(001) hybrid halide perovskite, was investigated using powder and single crystal x-ray diffraction, and x-ray photoemission spectroscopy. Single crystal x-ray diffraction studies indicate the methylammonium adopts multiple orientations within the crystal, at room temperature, evidence of both disordered methylammonium sublattice within a stiff and ordered PbBr₃ matrix lattice. Temperature dependent x-ray photoemission spectroscopy for bromine and lead core level peaks near the cubic to tetragonal I phase transition tend to support the characterization of methylammonium as a lattice polar liquid within the CH₃NH₃PbBr₃ crystal. The Br 3dₓ²ᵧ and Pb 4fₓ² core level Debye-Waller factor plots exhibited a temperature dependence indicative of an effective Debye temperature of 160±61K, while the Pb 4f₁/₂ core-level Debye-Waller factor plots...
show little temperature dependence, indicative of a very stiff lattice along the <001> direction. MAPbBr$_3$ satisfies the criteria for a lattice polar liquid and does not meet the criteria required for a ferroelectric material.

**11:30 AM ET05.01.07**

**Impact of Crystallographic Orientation Disorders on Electronic Heterogeneities in Metal Halide Perovskite Thin Films**

Benjamin Foley$^1$, Seung-Hun Lee$^2$, Kai Xiao$^2$, Benjamin Doughty$^1$, Yingzhong Ma$^4$ and Joshua Choi$^1$; $^1$University of Virginia, Charlottesville, Virginia, United States; $^2$Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Metal halide perovskite thin films have achieved remarkable performance in optoelectronic devices, but suffer from spatial heterogeneity in their electronic properties. To achieve higher device performance and reliability needed for wide-spread commercial deployment, spatial heterogeneity of optoelectronic properties in the perovskite thin film needs to be understood and controlled. Clear identification of the causes underlying this heterogeneity, most importantly the spatial heterogeneity in charge trapping behavior, has remained elusive. Here, a multimodal imaging approach consisting of photoluminescence, optical transmission, and atomic force microscopy is utilized to separate electronic heterogeneity from morphology variations in perovskite thin films. By comparing highly oriented and randomly oriented polycrystalline perovskite thin film samples, we reveal that disorders in the crystallographic orientation of the grains play a dominant role in determining charge trapping and electronic heterogeneity. This work also demonstrates a polycrystalline thin film with uniform charge trapping behavior by minimizing crystallographic orientation disorder. These results suggest that single crystals may not be required for perovskite thin film based optoelectronic devices to reach their full potential.

**11:45 AM ET05.01.08**

**Thermodynamic Stability of Perovskites—From Empirical Tolerance Factor to Machine Learning**

Wanjian Yin; Soochow Institute for Energy and Materials Innovations (SIEMIS), Soochow University, Suzhou, China.

Perovskite stability is of the core importance and difficulty in current research and application of perovskite solar cells. Nevertheless, over the past century, the formability and stability of perovskite still relied on simplified factor based on human knowledge, such as the commonly used tolerance factor $t$. Instead of $t$, we proposed a new factor ($\mu$+$\eta$), where $\mu$ and $\eta$ are the octahedral factor and the atomic packing fraction respectively. As a stability descriptor ($\mu$+$\eta$) is able to predict the relative stability among any two perovskites with the accuracy ~90%, much better than ~70% of $t$ [1,2].

We further combined machine learning (ML) with first-principles density functional calculations, proposed a strategy to calculate the decomposition energies, considered to be closely related to thermodynamic stability, of 354 kinds halide perovskites, established the machine learning relationship between decomposition energy and compositional ionic radius and investigated the stability of 14190 halide double perovskites. The ML model, which was trained based on the theoretical data, has been validated by experimental results of a series of rare earth metal halide perovskites (up to ~10$^3$ kinds), performs much better than descriptors such as tolerance factor $t$ and ($\mu$+$\eta$) and further provides elemental and concentration suggestion for improving the stability of mixed perovskite [3].


**SESSION ET05.02: Defects, Ion Motion and Polarization**

Session Chairs: Saiful Islam and Yabing Qi; Monday Afternoon, November 26, 2018
Hynes, Level 3, Room Ballroom B

**1:30 PM ET05.02.01**

**Ionic Transport, Defects and Electrooptical Response of Perovskite Solar Cells**

Juan Bisquert; Institute of Advanced Materials, Universitat Jaume I, Castello, Spain.

The development of organic-inorganic lead halide perovskites with very large efficiency requires us to understand the operation of the solar cell. This class of semiconductors presents remarkable bulk electronic and optical properties, but the contacts to the device are a key aspect of the operation and show important dynamic interactions. We describe the results of analysis of kinetic phenomena using frequency modulated techniques. First with impedance spectroscopy we provide an interpretation of capacitances as a function of frequency both in dark and under light, and we discuss the meaning of resistances and how they are primarily related to the operation of contacts in many cases. The capacitance reveals a very large charge accumulation at the electron contact, which has a great impact in the cell measurements, both in photovoltage decays, recombination, and hysteresis. We also shows the identification of the impedance of ionic diffusion by measuring single crystal samples. Working in samples with lateral contacts, we can identify the effect of ionic drift on changes of photoluminescence, by the creation of recombination centers in defects of the structure. We also address new methods of characterization of the optical response by means of light modulated spectroscopy. The IMPS is able to provide important influence on the measured photocurrent. We describe important insights to the measurement of EQE in frequency modulated conditions, which shows that the quantum efficiency can be variable at very low frequencies.

References


**2:00 PM ET05.02.02**

**From MAPbI$_3$ to Mixed-Cation Perovskites—Atomic-Scale Insights into Defects, Diffusion and Degradation**

Saiful Islam; University of Bath, Bath,
Polarization Process in Metal-Halide Perovskites

Suszanne Birkhold, Susanne Koch and Lukas Schmidt-Mende; University of Konstanz, Constance, Germany.

Perovskite semiconductors are a new class of semiconductors, significantly different from organic and also inorganic semiconductors. We have applied thermally stimulated current measurements to study the polarization processes of the organic cation in MAPbI₃ thin films across the orthorhombic to tetragonal phase transition. The nature of the cation polarization within the orthorhombic phase was found to be highly repeatable, with a separation of 20 K between polarization and depolarization processes, and was investigated with respect to its extrinsic polarizability by external electric fields. Our results show that the polarization of organic cations is correlated with a sudden improvement in solar cell performance and has impact on the working mechanisms of perovskite solar cells.

References

2:30 PM ET05.02.03
Polarization Process in Metal-Halide Perovskites

2:45 PM ET05.02.04
Huge Enhancement of Ion Conduction and Implications for Photo-Decomposition in Hybrid Organic-Inorganic Lead Halides Perovskite

3:00 PM BREAK

3:30 PM ET05.02.05
Advance in Understanding Defects and Passivation in Perovskite Materials and Devices

4:00 PM ET05.02.06
Quantification of Ion Migration in Halide Perovskites with Potassium Passivation

References

Advance in Understanding Defects and Passivation in Perovskite Materials and Devices

Jinsong Huang; University of North Carolina-Chapel Hill, Chapel Hill, North Carolina, United States.

Perovskite solar cells have entered a stage that serious consideration of their feasibility of commercialization with their fast increasing efficiency and stability. Nevertheless, the understanding of these materials has not keep the pace with the efficiency enhancement. In this talk, I will present our recent progress in understanding the materials and physics of polycrystalline perovskite solar cells. The charge recombination in the defective films will be analyzed, and passivation techniques which involves of different types of molecular structures will be presented. Starting from proposing the first passivation concept using fullerene early in 2014, we continue to strive for new passivation molecules to improve the passivation effect in terms of the amount and types of defects that can be passivated. I will also discuss the nature of the defects and passivation in perovskites which is very different from traditional semiconductors such as silicon.

Quantification of Ion Migration in Halide Perovskites with Potassium Passivation

Moritz H. Futscher1, Kangyu Ji2, Samuel D. Stranks2 and Bruno Ehrler1; 1AMOLF, Amsterdam, Netherlands; 2University of Cambridge, Cambridge, United Kingdom.

Solar cells based on halide perovskites show efficiencies close to highly-optimized silicon solar cells. However, ions migrating in these perovskites lead to device degradation and complicate the characterization of perovskite solar cells. We recently showed that transient ion-drift is a powerful method to quantify activation energy, concentration, and diffusion coefficient of mobile ions in perovskite solar cells. [1] By studying methylammonium lead triiodide (MAPbI₃) we could identify three migrating ion species which we attribute to the migration of iodide (I⁻) and methylammonium (MA⁺). We found that both MA⁺ and I⁻ ions migrate at room temperature, but at very different timescales (seconds and milliseconds respectively). These results suggest that the migration of MA⁺ ions is the major factor influencing current-voltage hysteresis in perovskite solar cells.

Recently it was shown that introducing potassium into triple-cation perovskites passivates surfaces and stabilizes luminescence without compromising charge transport or extraction. [2] This has been attributed to the mitigation of both non-radiative losses and ion migration in perovskite films. In these triple-cation perovskites with potassium passivation, we find that the activation energy of mobile anions is not influenced by potassium passivation, but that the concentration decreases and the diffusion coefficient increases with increasing potassium passivation. We furthermore find that injected charge...
carriers influence both the activation energy and the diffusion coefficient for mobile anions. This quantification of mobile ions in triple-cation perovskites will lead to a better understanding of ion migration and the influence of passivating agents on that migration.

References

4:15 PM ET05.02.07
Nature of the Ionic Charge Carriers in Methylammonium Lead Iodide Alessandro Senocrate1,2, Gee Yeong Kim1, Igor Moudrakovski1, Tae-Youl Yang1, Giuliano Gregori1, Michael Graetzel1 and Joachim Maier1; 1Max Planck Institute for Solid State Research, Stuttgart, Germany; 2École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

A pertinent investigation of the exceptional photoelectrochemical properties of halide perovskites has to consider the significant ion transport present in these materials.1,2 Such transport gives rise to bulk and boundary polarization phenomena during operation, and it is also relevant for the degradation kinetics of halide perovskites materials and related photovoltaic devices.3,4 In this contribution we analyze the nature of the ionic conductivity in methylammonium lead iodide, the archetypal hybrid halide perovskite, by means of various electrical, electrochemical and nuclear magnetic techniques.5,6 Under equilibrium conditions, iodine vacancies are unambiguously shown to be the dominant ionic carriers, while electron holes dominate the electronic conductivity at high (and excess electrons at low) iodine activities. The contributions of methylammonium and lead ions, instead, are small (upper limits are given). As a follow-up, we discuss the changes of the various charge carrier concentrations as a function of the decisive control parameters (stoichiometry and doping content).6,7 Based on these equilibrium considerations, we can also discuss the charge carrier chemistry under illumination where not only electronic, but also ionic conductivity are largely enhanced.7

References

4:30 PM ET05.02.08
Highly Stable Perovskite Solar Cells via Controlling Ions/Charges/Molecules Diffusion Xudong Yang1,2, Han Chen1 and Liyuan Han2; 1State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai, China; 2Research Network and Facility Services Division, National Institute for Materials Science, Tsukuba, Japan.

Organic-inorganic hybrid perovskite solar cells (PSCs) are promising low-cost photovoltaic technology owing to the high energy conversion efficiency. However, the device stability has a large gap to the ideal level for future application. Here I would like to introduce our recent approaches in achieving highly stable PSCs. We proposed a strategy to control the diffusion of ions/charges/molecules by developing nano-carbon electron transporting layer in p-i-n structure perovskite solar cells. It successfully enabled better stability because the diffusion of iodide within the device was hindered before it induced corrosion of the metal electrode while the diffusion of electrons was improved. We further control the ions/charges/molecules diffusion within n-i-p structure perovskite solar cells. The ions diffusion was reduced to decrease the charge trap states when the device was aging. This helped to obtain device with excellent stability and high efficiency. The device performance was certified by a public test center with the record of certified stabilized power output.

References

4:45 PM ET05.02.09
Impact of Thin-Film Perovskite Composition on Sub-Band Gap Absorption Due to Defect States Biwas Subedi, Chongwen Li, Cong Chen, Maxwell Junda, Dewei Zhao, Yanta Yan and Nikolay Podzorov; Physics and Astronomy, University of Toledo, Toledo, Ohio, United States.

Organic-inorganic halide ABX3 (A: methylammonium—MA, formamidinium—FA, Cs; B: Pb, Sn; X: I, Br) perovskites currently serve as absorber materials in highly efficient solar cells. Preparation of films which are highly crystalline, defect free; stable against heat, light, and moisture; and with desired optoelectronic properties are present challenges. Cationic and anionic alloying / doping has been shown to improve phase stability, increase grain size and uniformity, and reduce sub-bandgap absorption and recombination due to defects to improve solar cell performance. A combination of photothermal deflection spectroscopy, spectroscopic ellipsometry, and unpolarized transmittance measurements of solution processed perovskite thin films prepared with mixed cation/anion composition are used to study the impact of these variations on sub-bandgap absorption due to defects. In particular, Urbach energies from sub-band gap absorption are correlated with structural, electrical, above band gap optical properties, and device performance. As an example of A-cation substitution, replacing 0.4 FA with MA in x = 0.15 FASn0.5Pb0.5I1-xBrx reduces Urbach energies from 53 to 26 meV and is accompanied by increased grain size, reduced defect density, and improved electronic properties. For anion substitution, I to Br ratios in FASn0.5Pb0.5I1-xBrx (x ≤ 0.15) show materials prepared with x ≤ 0.04 having the lower Urbach energy than higher Br content. In FASn0.5PbI3, Urbach energies are reduced from lead thiocyanate (Pb(SCN)2) treatment and solvent annealing preparation. Links will be established between the particular cation/anion composition configurations currently used in solar cell device grade perovskite films, structural and electrical properties, and the associated sub-bandgap absorption characteristics. Further expansion of these studies will help to more fundamentally understand the defect states present in particular compositions and to identify practical pathways to improvements in stability and electronic quality for experimentally produced perovskite thin films used as solar cell absorbers.
ET05.03.01
Interface Engineering to Improve Efficiency and Operational Lifetime of Perovskite Solar Cells Longbin Qiu, Luis K. Ono, Yan Jiang, Matthew R. Leyden, Sonia R. Raga, Shenghao Wang and Yabing Qi; Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), Okinawa, Japan.

Operational lifetime is one of the main challenges for perovskite solar cells towards commercialization [1]. Other than the stability of perovskite materials themselves [2], the operational lifetime issue may also come from several other factors, including the interface with perovskite and the electrodes being used [3-5]. Interface engineering is expected to not only improve the performance, but also to increase the operational lifetime of the devices. In this work, we modify electrode transport layer (ETL) surface with an interfacial layer to prevent interaction between ETL and CH3NH3PbI3 [6]. This strategy indeed leads to significantly improved operational lifetime of our devices. We show that it is necessary to consider not only the band alignment at the interface, but also interface chemical interactions between the thin interface layer and the perovskite film.


ET05.03.02
General Nondestructive Post-Treatment to Passivate Perovskite Solar Cells with Enhanced Stability and Performance Shenghe Zhao, Jiangsheng Xie, Han Wang, Jianbin Xu and Keyou Yan; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Hybrid perovskite thin films have many potential areas at surface and interface during the film formation, which degrade the stability and photovoltaic performance. Passivation via post-treatment can enhance the film quality, but present methods are slightly destructive to three-dimensional perovskite (3DP) due to the solvent effect, which hinders fabrication reproducibility. Herein, we demonstrate that 4-fluoroaniline (FAL) is an effective antisolvent candidate for surface/interface passivation and thus nondestructive during the fabrication. Density functional theory (DFT) calculation reveals that the antisolvent and non-destructive properties are attributed to the conjugated amine in aromatic ring. Hot vapor assisted colloidal process (HVACP) is employed for the post-treatment. The molecular passivation yields an ultrathin protection layer with hydrophobic fluorine tail and thus enhances the stability and optoelectronic properties. FAL perovskite solar cell (PSC) delivers 20.48% power conversion efficiency (PCE) in the ambient condition. Micro-photoluminescence reveals that passivation activates dark defective state at the surface and interface, delivering the impact picture of boundary on the local carriers. Different from previous passivation reagents, FAL is suitable for post-treating various perovskites and healing the defects via a simple process, without destructiveness to pristine perovskite. Therefore, this work demonstrates a generic nondestructive chemical approach for improving the performance and stability of PSC.

ET05.03.03
Enlarging the Grain in Low-Temperature Solution Processed Perovskite Films Using Simple Annealing Method Md Wavesh Qarony1, Sainan Ma1, Mohammad I. Hossain1, Chu Tung Yip2 and Yuen H. Tsang1; 1Department of Applied Physics and Material Research Center, The Hong Kong Polytechnic University, Kowloon, Hong Kong; 2Department of Physics, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen, China.

Perovskites have recently attained great attention owing to its excellent electronic and optical properties. The optoelectronic properties can be further tailored according to the needs of applications. It is demonstrated that perovskites photovoltaic devices with a theoretical energy conversion efficiency limit of 31% can be realized if large grain size with uniform intra-grain and inter-grain crystallinity are ensured [1-2]. However, achieving a good crystallinity along with larger grain is an insurmountable task. Herein, a uniform and large grain size of max approx. 3 µm is demonstrated for two steps solution process of MAPbI3 perovskites at 100°C using a simple annealing method. The annealing time duration varies from 1 hour to 24 hours long, while the grain size gradually increases with the prolongation of the annealing time. However, the grain size remains almost constant when the annealing time longer than 12 hours. Furthermore, a distinctly larger grain size of max. about 6 µm is also exhibited for the same perovskite film deposited on a PbI2 seed layer prepared by chemical vapor deposition method. An optical measurement is being carried on with some initial promising results to characterize the photocurrent loss and recombination center on the grain boundaries, intra-grain, and inter-grain scale of perovskites using femtosecond laser of confocal microscope. The investigations on such microcrystalline perovskites with large grains are highly essential for conducting electronic and optical measurements to enhance the performance of perovskite devices.

Acknowledgement: This work was financially supported by a grant from Shenzhen Municipal Science and Technology projects (Grant No. 201605313001154) and The Hong Kong PhD Fellowship Scheme supported by the Hong Kong RGC.

Reference:

ET05.03.04
Functional Conjugated Ligands Assisted Charge Transport Between Coupling Colloidal Perovskite Quantum Dots Jinfei Dai, Yifei Shi, Jie Xu, Lin Zhang and Zhaoxin Wu; Xi’an Jiaotong University, Xi’an, China.

Conventionally, in preparing stable colloidal quantum dots (QDs), long hydrocarbon chains capping ligands such as n-octylamine (OA) are indispensable. However, the commonly used long hydrocarbon capping ligands are always insulator and block efficient carrier transport between QDs, leading to inferior
performance of light-emitting diode (LED), and other optoelectronic devices. Until now, ligand exchange, reducing ligand chain length and ligand density control are adopted to improve the film conductivity of QDs, but still didn’t break the dilemma of the trade-off between the film conductivity and colloidal stability of QDs. In this work, for the first time, we overcome this dilemma, successfully synthesized methylamine lead bromide (MAPbBr3) QDs with an unsaturated conjugated alkyl-amine, 3-Phenyl-2-propan-1-amine (PPA), as ligand. Owing to the denser electron cloud overlapping and delocalization effect of conjugated molecules, PPA effectively improves the conductivity of QDs film without compromising its colloidal stability. With analogous quantum photoluminescence yield and stability of OA-capped MAPbBr3 QDs, films of PPA-capped MAPbBr3 QDs show high electronic conductivity, which carrier mobility is nearly increased 22 times of that of OA-capped MAPbBr3 QDs films. As an example of application in LEDs, the QD-LED based on PPA-capped MAPbBr3 QDs exhibited a maximum luminance of 9052 cd m⁻² and a maximum current efficiency of 9.08 cd A⁻¹, which is 8 times of that of QD-LED based on OA-capped MAPbBr3 QDs (1.14 cd A⁻¹). This work provides critical solution for the poor conductivity of QDs in applications of energy-related devices DOI: 10.1002/anie.201801780

**ET05.03.05**

**Bulk Heterojunction Quasi-Two-Dimensional Perovskite Solar Cell with 1.18 V High Photovoltage**

Han Wang, Jiangsheng Xie, Shenghe Zhao, Jianbin Xu and Keyou Yan; The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Multicomponent quasi-two-dimensional perovskites (Q2DPs) have efficient luminescence and improved stability, which are highly desirable for light emitting diode (LED) and perovskite solar cell (PSC). However, the lack of radiative recombination at room temperature is still not well understood and the performance of PSC is not good enough as well. The open-circuit voltage ($V_{OC}$) is even lower than that of 3D PSC with narrower band gap. In this work, we study the energy transfer of excitons between their multiple components by time-resolved photoluminescence (TRPL) and find that charge transfer from high energy states to low energy state is greatly suppressed at elevated temperature due to increasing trap-mediated recombination. This may reveal the bottleneck of luminescence at room temperature in Q2D-2D, leading to large photovoltage loss in PSC. Therefore, we develop a p-i-n bulk heterojunction (BHI) structure to reduce the nonradiative recombination. We obtain high $V_{OC}$ of 1.18 V for (PMA)$_3$MA$_5$Pb$_{33}$Cl$_7$ (N = 5) in PSC, much higher than the planar counterparts. The enhanced efficiency is attributed to the improved exciton dissociation via BHI interface. Our results provide an important step towards high $V_{OC}$ and stable 2D PSCs, which could be used for tandem solar cell and colorful photovoltaic windows.

**ET05.03.06**

**Two-Dimensional Hybrid Dion-Jacobson Perovskites for Solar Cell Application**

Lingling Mao¹, Weijun Ke¹, Laurent Pedesseau², Claudine Katar³, Jacky Even², Constantinos Stoumpos⁴ and Mercouri G. Kanatzidis⁴; ¹Chemistry, Northwestern University, Evanston, Illinois, United States; ²Univ Rennes, Rennes, France.

Hybrid organic-inorganic perovskite material has emerged as one of the most promising semiconducting materials for optoelectronic applications. The power conversion efficiency (PCE) of the three-dimensional (3D) perovskite based solar cell has achieved 22%. With a higher flexibility in structural engineering, the two-dimensional (2D) perovskite not only allows for property tuning in a broader sense, but also demonstrates higher stability in devices compared to the 3D perovskite. Here, we present the first complete series of the Dion-Jacobson phases in the halide perovskite family, incorporating the 3-(aminomethyl)pyridinium (3AMP) or 4-(aminomethyl)pyridinium (4AMP) as spacers cations. The general formula for the DJ perovskite is $A^+$\(_{n\times2}\)\(\text{Pb}_\text{n+1}^\text{2+}\text{X}_\text{n+1}\) (3AMP) or $A^+$\(_{n\times2}\)\(\text{Pb}_\text{n+1}^\text{2+}\text{X}_\text{n+1}\) (4AMP) (3AMP) or 4-aminomethylpyridinium (4AMP) as spacers cations. The general formula for the DJ perovskite is $A^+$\(_{n\times2}\)\(\text{Pb}_\text{n+1}^\text{2+}\text{X}_\text{n+1}\). Compared with the Ruddlesden–Popper (RP) phases, the DJ perovskite only has one sheet of organic cations in between the layers, resulting in much closer interlayer distance (~4Å). The inorganic layers in the DJ phases are stacking perfectly on top of each other with no displacement. With a slight modification on the organic cation (3AMP vs. 4AMP), the optical properties are heavily influenced by the distortion of the inorganic layers, as the 3AMP series (less distorted) has narrower band gaps than the 4AMP series (more distorted). We further demonstrate their difference in solar cell devices, as the (3AMP)(MA)\(_3\)(PbI\(_4\)) has the best PCE of 7.3%, much higher than the corresponding (4AMP)(MA)\(_3\)(PbI\(_4\)). With compositional engineering on the existing system, we optimize the device performance of (3AMP)(MA)\(_3\)(FA\(_{0.25}\))(PbI\(_4\)) (FA = formamidinium) to 12.0%. The new DJ system highlights the crucial role of functional organic cations in the 2D hybrid perovskite, where they influence the overall property of the material by interactions with the inorganic framework, which ultimately affect the device performance.

**ET05.03.07**

**Unveiling the Room Temperature Low-Threshold Amplified Spontaneous Emission in All-Inorganic Perovskite Thin Films by Dual Source Thermal Evaporation**

Lin Zhang, Zhaoxin Wu, Hua Dong, Jinfei Dai and Xiaoyun Liu; Xi’an Jiaotong University, Xi’an, China.

Recent years have witnessed rapid development of halide perovskite as a new class of optical-gain media for lasing applications. Driven by the rapidly increased research on organic-inorganic perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Cl, Br, I}$) (Science, 356, 1376 (2017)), inorganic perovskite CsPbX$_3$ has also attracted high attention because it shows increased air-stability (Nat. Commun. 8, 15640 (2017), Nat. Photon. 11, 108 (2017)). For achieving amplification spontaneous emission (ASE) with low threshold from perovskite thin films, ultra-compact grains and smooth morphology are prerequisites. Meanwhile, the prepared perovskite thin films have good photo and environmental stability under ambient conditions is also paramount. However, the solution-processed thin films generally difficult to control perovskite crystallization and film quality due to low solubility of the cesium bromide (CsBr) precursor, result in inevitable large pinholes and poor surface coverage (Nat. Commun. 6, 8056 (2015)). Such defects may result in reduced optical confinement effect and poor ASE from the perovskite films, seriously affecting their lasing performance.

To solve these issues, herein, we demonstrate that by dual source thermal evaporation which enables the attainment of nearly pinhole-free thin films, inorganic perovskite (such as CsPbX$_3$ or CsSnX$_3$) films exhibit enhanced crystallization, improved photoluminescence (PL) uniformity and intensity, and long-term reliability. The ASE with improved emission intensity and reduced threshold from evaporated thin film were demonstrated in our previous works (J. Phys. Chem. C, 28, 121 (2017); PSS RRL, 5, 12, (2018)). Notably, the annealed CsPbBr$_3$ thin films fabricated by thermal evaporation exhibit ultralow ASE threshold of ~ 3.3 μJ/cm², enhanced crystallization, improved surface morphology and gain coefficient above 300 cm⁻¹. Stable ASE intensity without degradation for at least 7 hours is observed under continuous excitation under ambient conditions. Meanwhile, a Fabry-Perot (F-P) cavity laser based on unannealed CsPbBr$_3$ thin film, featuring ultralow threshold and directional output is also realized. Our works advocate that the perovskite thin films possess excellent film morphology and excellent long-term stability which prove to be critical to enhance ASE and lasing performance, as well as highlights the feasibility of evaporated CsPbBr$_3$ thin films as practical optical gain media for the future light-emitting applications.

**ET05.03.08**

**First Principle Polaron Modeling in Hybrid Perovskites Using the GGA+U Method**

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Organohalide lead hybrid perovskites (HPs) have become the benchmark, state-of-the-art materials in third generation, perovskite solar cell devices, achieving a power conversion efficiency of over 22%. Yet, the underlying photo-physical properties of HPs are still under debate. Here we use density functional theory within the generalized gradient approximation with a Hubbard correction (GGA+U) to study structural properties, band structures, charge carrier dynamics and electron-phonon coupling in HPs with different compositions. Our preliminary DFT+U simulations reveal the formation of light-induced self-trapped hole polarons in HPs with different halides, which may have profound implications on charge transport, recombination, and experimentally observed device instability under illumination. Moreover, we argue that polaron induced loss of inversion symmetry and enhanced Rashba splitting might be responsible for our recent experimentally observed room-temperature ultrafast photocurrent and free-space terahertz emission generation from unbiased CH3NH3PbI3 benchmark HPs. Polarization dependence of the observed photoresponse is consistent with the Bulk Photovoltaic Effect caused by a combination of injection and shift currents. Ballistic by nature, these photocurrents may enable next generation perovskite solar cells with efficiency that can theoretically exceed the Shockley–Queisser limit. We also developed a computational method that allows estimating the polaron size, while minimizing self-interaction errors, as well as the overall computational requirement of each calculation.

ET05.03.09
Stabilization of Cubic Crystalline Phase in Organometal Halide Perovskite Quantum Dots via Surface Energy Manipulation
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Surface functionalization of nanoscale materials has significant impacts on their properties due to their large surface-to-volume ratio. In this work, we studied temperature dependent crystal phase transitions in CH3NH3PbBr3 Perovskite quantum dots (PQDs) ligated with octylammoniumbromide (P-OABr) and 3-aminopropyl triethoxysilane (P-APTES), using a framework of static and dynamic spectroscopy. P-OABr undergoes the expected structural phase transition from tetragonal to orthorhombic phase at ~140 K, established by the emergence of a higher energy band at 2.64 eV in the photoluminescence (PL) spectrum, while no phase transition was observed in the case of P-APTES. Such phase stabilization is a result of variation in their respective surface energies, an important contributing factor to the Gibbs free energy for nanomaterials. On further investigating the consequences of this altered crystal phase diagram using time-resolved PL, excitation power dependent PL and Raman microscopy over a range of 300 – 20 K, we observe significant differences in recombination rates and charge carrier types between P-APTES and P-OABr. Our findings highlight how aspects of PQD phase stabilization are linked to nanoscale morphology and the surface energy manipulation of the crystal phase diagram, providing critical insights into the synthesis of stable perovskite crystals for solar energy conversion and other applications such as light emitting diodes.

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ET05.03.10
Controlled Homoepitaxial Growth of Hybrid Perovskites
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Organic–inorganic hybrid perovskites have demonstrated tremendous potential for the next-generation electronic and photovoltaic devices due to their remarkable carrier dynamics. Current studies are focusing on polycrystals, since controlled growth of device compatible single crystals is extremely challenging. Here, the first chemical epitaxial growth of single crystal CH3NH3PbBr3 with controlled locations, morphologies, and orientations, using combined strategies of advanced microfabrication, homeopitaxy, and low temperature solution method is reported. The growth is found to follow a layer-by-layer model. A light emitting diode array, with each CH3NH3PbBr3 crystal as a single pixel, with enhanced quantum efficiencies than its polycrystalline counterparts is demonstrated.

ET05.03.11
High Stability and Ultralow Threshold Amplified Spontaneous Emission from Formamidinium Lead Halide Perovskite Films
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The opportunity of lasing from organolead halide perovskite materials has recently attracted extensive attention in order to realize electrically driven lasers. So far, for devices with planar structure, most reports focus on CH3NH3PbI3 (MAPbI3) films, which are unstable when in operation due to phase transitions and elemental redistribution. Herein, we demonstrate highly stable amplified spontaneous emission (ASE) with ultralow threshold from formamidinium-based perovskite CH(NH2)2PbI3 (FAPbI3) films. ASE from MAPbI3-stabilized FAPbI3 films was also achieved, with an ultralow threshold of about 1.6 μJ/cm². More importantly, upon continuous operation under pulsed laser for several hours, the ASE intensity in the MAPbI3 film decreased to 9% of the initial value, while it was maintained above 90% in the FAPbI3 film. The low trap density, smooth film morphology, high thermal stability, and the excitonic emission in nature of the FAPbI3 film are expected to contribute to its low lasing threshold and high stability, demonstrating a strong potential for applications in continuouswave pumped lasers and electrically driven lasers.

ET05.03.12
A Novel Series of Quasi-2D Ruddlesden-Popper Perovskites Based on Short-Chained Spacer Cation for Enhanced Photodetection
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Quasi two-dimensional (2D) layered organic-inorganic perovskite materials (e.g. (BA)2(MA)n-1PbnI3n+1; BA = butylamine; MA = methylamine), have recently attracted a wide attention due to their superior moisture stability as compared with three-dimensional counterparts. Inevitably, hydrophobic yet insulating long-chained organic cations improve the stability at the cost of hindering charge transport, leading to the unsatisfied performance of subsequently fabricated devices. Here, we report the synthesis of Quasi-2D (iBA)2(MA)n-1PbnI3n+1 perovskites, where the relatively pure phase (iBA)2PbI4 and (iBA)2MA2PbI6 films can be obtained. Because of the shorter branched-chain of iBA as compared with that of its linear equivalent (n-butylamine, BA), the resulting (iBA)2(MA)n-1PbnI3n+1 perovskites exhibit much enhanced photodetection properties without sacrificing their excellent stability. Through hot-casting, the optimized (iBA)2(MA)n-1PbnI3n+1 perovskite films with n = 4 give the significantly improved crystallinity, demonstrating the high responsivity of 117.09 mA/W, large on-off ratio of 4.0×105 and fast response speed (rise and decay time of 16 ms and 15 ms, respectively). These figure-of-merits are comparable or even better than those of state-of-the-art Quasi-2D perovskites-based photodetectors reported to date. Our work not only paves a practical way for future perovskite photodetector fabrication via modulation of their intrinsic material properties, but also provides a direction for further performance enhancement of other perovskite optoelectronics.

ET05.03.13
Hybrid Organic-Inorganic Lead Halide Perovskites Investigated by Modulated Surface Photovoltage Spectroscopy
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Hybrid organic-inorganic lead halide perovskites have emerged as a new group of materials for highly efficient solar cells (SCs) based on earth abundant elements which can be processed from solutions at low temperature. CH$_3$NH$_3$Pb(I$_{1-x}$Br$_x$)$_3$ perovskite films were studied since it belongs to the materials which are of great interest for top SCs in tandem SCs with c-Si bottom SCs due to its tunable band gap. Electronic properties of CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbBr$_3$, perovskite films sensitively depend on crystallization and defect formation and are crucial for the performance and stability of SCs. The band gap ($E_g$), exponential tail states ($E_T$) and the diffusion length ($L$) are decisive parameters for absorbers in SCs since they give principle limitations for photogeneration and Fermi-level splitting. In CH$_3$NH$_3$PbI$_3$ perovskites, $E_T$, $E_g$ and $L$ are not necessarily constant and can depend, for example, on the preparation conditions and degradation. Therefore, $E_T$, $E_g$ and $L$ of CH$_3$NH$_3$PbI$_3$ perovskites were studied with respect to stoichiometry, interfaces, degradation and temperature. Modulated SPV spectroscopy allows for the contactless and very sensitive characterization of $E_T$, direction of charge separation and L (after Goodman) without the requirement of the preparation of contacts after or during different stages of layer preparation, light soaking etc. Vegard’s law was applied to obtain the composition of CH$_3$NH$_3$PbI$_3$($1_x$Br$_x$)$_3$. The $E_g$ of CH$_3$NH$_3$PbI$_3($1_x$Br$_x$)$_3$ films varied between 1.59 eV to 2.30 eV depending on the stoichiometry whereas the bowing parameter was 0.36 eV. The influence of the substrate on $E_T$ and $E_g$ of CH$_3$NH$_3$PbI$_3$ films was investigated. It has been found, for example, that $E_T$ and $E_g$ of CH$_3$NH$_3$PbI$_3$ sensitively depend on the substrate and on soaking in nitrogen atmosphere and that light soaking has strong influence on the direction of modulated charge separation. CH$_3$NH$_3$PbI$_3$ deposited on double layers of TiO$_2$/PCBM and SnO$_2$/PCBM showed a constant band gap of 1.58 eV and a low scatter in $E_T$. This was attributed to the modification of the TiO$_2$ or SnO$_2$/CH$_3$NH$_3$PbI$_3$ interfaces by PCBM allowing for efficient charge separation and transfer and well reproducible conditions for the layer formation. A decrease of $L$ with light soaking was observed and can be attributed to light induced degradation due to charging and discharging of trap states and formation of defects at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface. Furthermore, $E_T$ and $E_g$ of CH$_3$NH$_3$PbI$_3$ stabilized with PMMA increased with increasing temperature, i.e. thermal expansion gives the predominant contribution to the temperature dependence of $E_T$ of CH$_3$NH$_3$PbI$_3$ whereas dynamic disorder was limited by phonons. A jump-like increase of $E_T$ in the region of phase transition was attributed to the phase transition from the tetragonal to the cubic phases.

**ET05.03.14**

**In Situ Grain Encapsulation for Stable Formamidinium-Based Perovskite Solar Cells**

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Owing to the wide absorption range and high thermal stability, formamidinium (FA) based lead iodide perovskites have recently emerged as the most promising light-absorber materials for photovoltaics. However, they suffer from fast degradation to undesirable non-perovskite polymorphs in the ambient atmosphere, which retards the real-world application of FA-based PSCs. Herein, a new strategy of in situ grain encapsulation is demonstrated to address this issue. This strategy is realized by co-addition of tetraethylorthosilicate (TEOS) and H$_2$O into the perovskite precursor solution. The hydrolysis of TEOS produces silica oligomers in the precursor solution. Driven by the perovskite crystallization, silica fills in the grain boundaries and covers the surfaces of perovskite grains, forming encapsulating layers at the “grain”-scale. Silica protects perovskite grains from the ambient air, thus improving the stability. Furthermore, $E_T$ and $E_g$ of CH$_3$NH$_3$PbI$_3$ stabilized with PMMA increased with increasing temperature, i.e. thermal expansion gives the predominant contribution to the temperature dependence of $E_T$ of CH$_3$NH$_3$PbI$_3$ whereas dynamic disorder was limited by phonons. A jump-like increase of $E_T$ in the region of phase transition was attributed to the phase transition from the tetragonal to the cubic phases.

**ET05.03.15**

**Modification of Excitonic Properties of Halide and Mix-Halide Hybrid Perovskite Thin Films Using Interface Engineering**

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Zinc oxide (ZnO) substrates of varying morphologies, including single crystalline (SC), micro-structured (MS) and nanostructured (NS) substrates, are interfaced with pure (CH$_3$NH$_3$PbI$_3$) and mixed (CH$_3$NH$_3$PbI$_3$:CH$_3$NH$_3$PbBr$_3$) perovskite thin films. The perovskite/ZnO interfaces are characterized by means of electron microscopy correlated with charge transfer absorption which are probed by temperature, power, time-resolved photoluminescence (PL) spectroscopy. SC-ZnO acts as an effective electron extraction layer as evidenced by PL quenching, reduced exciton density and recombination lifetime in the perovskite thin film. On the other hand, MS-ZnO is observed to result in a mild increase of the PL intensity of the perovskite film at room temperature, and NS-ZnO further results in PL intensity enhancement by up to a factor of thirty thousand and increase of recombination rates by 50%. These trends vary with temperature, and our results demonstrate the critical role played by morphology of the underlying substrates in charge dissociation and extraction in perovskite thin films. We conclude that while SC-ZnO can be implemented as an electron extraction layer in photovoltaic devices, MS- and NS-ZnO can be incorporated as scaffold in optical devices that require high quantum yield. This work was supported by NASA MIRO grant No. NNX15AQ01A.

**ET05.03.16**

**Discovery of the 2D Mixed Halide Perovskites A$_2$Bi$_2$Cl$_6$ (A = Cs, Rb)—Exploring the Limits of the Defect Perovskite Structure**

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Halide perovskites have remarkable optical properties which enabled their success as solar cells, with device efficiencies quickly rising above 22%. Perovskites have the formula AMX$_3$, where A is a large cation occupying voids between a corner-connected framework of MX$_6$ octahedra. Much of this work is based on the organic-inorganic CH$_3$NH$_3$PbI$_3$ and HC(NH$_2$)$_3$PbI$_3$, however these hybrid perovskites are limited by stability issues which have led researchers to pursue all-inorganic compositions. The tolerance factor of the 3D structure limits the number of such compounds, prompting the extension of the perovskite structure to other main group metals such as Bi$^{3+}$ and Sb$^{3+}$ which retain the ns$^2$ lone pair that plays an important role in the halide perovskite electronic structure.

One structure family that maintains a corner-connected MX$_6$ octahedral framework with trivalent M$^{3+}$ are the defect perovskites A$_3$M$_2$X$_9$. We have been investigating the optoelectronic properties of the iodide defect perovskite A$_3$M$_2$I$_9$ (A = Cs, Rb; M = Sb, Bi), finding that these four compounds have strong electronic-phonon coupling that results in self-trapped exciton photoluminescence (PL). They also show promise as semiconductor radiation detectors, with each responding to alpha particle irradiation. However, the A$_3$M$_2$I$_9$ are not entirely isostructural. The archetypical structure is a trigonal 2D bilayer that can be viewed as a (111) slicing of the AMX$_3$ structure, caused by an ordered vacancy on every third M site. In contrast, Cs$_2$Bi$_3$I$_9$ has a 0D dimer structure of isolated Bi$_4$I$_6$ biotahedra, while Cs$_2$Sb$_3$I$_9$ can form either of these structures depending on preparation method. Even the 2D Rb$_2$M$_2$I$_9$ compounds have distorted octahedra which lower the symmetry to monoclinic. To evaluate the size requirements that govern structure in this family, we modified these 2D and 0D structures using mixed halides.

We found that addition of Cl in a 1:2 ratio with I induced the trigonal 2D structure from the 0D Cs$_2$Bi$_3$I$_9$, resulting in the novel 2D defect perovskite
Enhanced Performance of Highly Efficient Formamidinium-Based Perovskite Light-Emitting Diodes via Rubidium Incorporation

Yifei Shi, Zhaoxin Wu, Jinfai Dai, Jie Xu and Ting Lei; Xi'an Jiaotong University, Xi'an, China.

Recently, organometal halide perovskites as promising candidates for light-emitting diodes have been studied greatly. However, for light-emitting application, the low photoluminescence quantum yield (PLQY) of OHPs film is critical to hinder the efficiency improvement of OHP film based light emitting diodes (PeLEDs). Although OHPs exhibit high photoluminescence quantum yield (PLQY>90%) in solution for nanocrystals or quantum dots, PLQY of OHPs is rather low in film state, which is a fatal limit for the high performance of PeLEDs.

To improve the PLQY of perovskite film, low dimensional perovskites were proposed to achieve high PLQY perovskite film. Nevertheless, the long-chain alkyl halides are indispensable to form quasi-2D structure, in which the insulative ligands will restrict the conduction of perovskite films and hamper the movement of carriers. In addition, partial substitution of A-site (ABX3) cations is an effective method to stabilize the crystal lattice and improve the optoelectronic properties, and design optimized solar cells involving these materials.

To pursue other better suitable A-site substitute cations is desirable for the higher performance of PeLEDs. Owing to RbBr exhibits higher solubility than CsBr in solvent, we select RbBr as dopant to incorporate into FAPbBr3 perovskite film. The optimal PeLEDs with 7% Rb incorporation exhibit a maximum reported luminance of 65535 cd/m2, EQE of 7.17% and a highest efficiency of 24.22 cd/A, the maximum luminance and current efficiency is enhanced by ~10 fold and ~5 fold compared to the controlled device, respectively. The enhanced device performance can be attributed to the site of FA+ partially, and distorts the crystal structure of FAPbBr3, thus affects the photovoltaic properties of FAPbBr3, in turn, improves the PLQY of perovskite films and decreases trap density of films. In addition, a little bit of Rb incorporation will not restrict the conduction of perovskite films. The Rb incorporation provides a new way to tune optical spectra, increase PLQY of perovskite film, and enhance the performance and stability of device.
Low-dimensional halide perovskites have recently attracted intense interest as alternatives to the three-dimensional (3D) perovskites because of their greater tunability and higher environmental stability. Herein, we present the new homologous two-dimensional (2D) series (NH3CmH2mNH3)((CH3NH3)n-PbI3-n)(n = 1 - 4), where m represents the carbon-chain number and n equals layer-thickness number. Multilayer (n > 1) 2D perovskites incorporating diammonium cations were successfully synthesized by solid state grinding method for n = 4 and 6, and by solution method for n = 7 - 9. Structural characterization by single-crystal X-ray diffraction for the m = 8 and m = 9 series (n = 1 - 4) reveals that these compounds adopt the space group of Cc for even n members and Pn̅c for odd n members. The optical bandgaps are 2.15 eV for two-layer (n = 2), 2.01 eV for three-layer (n = 3) and 1.90 eV for four-layer (n = 4), all behaving as direct bandgap semiconductor, also confirmed by DFT calculations. The materials exhibit excellent solution processability and casting the materials of n = 3 into thin-films was successfully accomplished. The films show a clear tendency for the higher-m members to have preferred orientation on the substrate, with m = 8 exhibiting almost perfect vertical layer orientation and m = 9 displaying both vertical and parallel layer orientation, as confirmed by GIWAXS measurements. The vertical layer orientation for the (NH3CmH2mNH3)((CH3NH3)n-PbI3-n) m = 8 member results in the best thermal, light and air stability within this series, thus showing excellent potential for solar cell applications.
Organic-inorganic halide perovskites have been attracting attention as materials for light-emitting diodes (LEDs) due to unique emission properties, which include high color purity with a very narrow emission and tuning the emission wavelength easily through the adjustment of the halide components, covering the entire range of visible light. However, one roadblock to LED application is the low exciton binding energy, which results in low luminescent efficiencies. One of the proposed strategies to enlarge the exciton binding energy is reduction of the dimensionality of the perovskite crystal structure. Here, we report highly luminescent thin films of formamidinium (FA) lead bromide perovskite (photoluminescence quantum yield, PLQY = 35.7%) via the formation of low dimensional architectures. A mixture of 3D FAPbBr3 and a new type of 2D perovskite FA2PbBr6 intercalated with dimethyl sulfoxide (DMSO) was formed by controlling the molar ratio of FAPbBr3 in the precursor solutions and annealing condition. A type I band alignment between the lower bandgap 3D FAPbBr3 and the higher bandgap 2D FA2PbBr6 was supported by density functional theory (DFT) calculations, which results in excitation confinement in the 3D phase and a substantial increase in PLQY. The composite films also exhibited excellent air and thermal stability. Details of analysis will be presented and discussed.

ET05.03.25
Ultra-High Purity, Monocrystalline Quality Hybrid Perovskite Thin Sheets for Radiation Detectors
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Halide perovskite materials synthesized via cost-effective solution process recently emerged as a promising candidate for detection of X-ray and gamma-ray. This is because of their high radiation absorption cross section in presence of heavy elements in the lattice, long mobility-lifetime product, balanced carrier mobility, which leads to high detectivity and energy resolutions. The current challenge is to synthesize large-scale high quality single crystals with minimal structural defects in both of bulk and surface. In this study, we report high quality Methylammonium Lead Bromide (MAPbBr3) single crystals that are prepared via modified inverted temperature crystallization (ITC) approach from precursor solution. With balanced crystalline-rate and proper choice of growth volume, we obtain mono-crystal with well controlled thickness from 400 nm up to 10 μm. Obtained mono-crystals demonstrate high material quality by the narrow peak width of X-ray diffraction (XRD) spectra that is comparable to the values reported for its bulk single crystals via ITC. In addition, the surface roughness is an order of magnitude lower compared to the bulk counterpart with homogenous surface charge distribution. Our high quality crystals with smooth surface are fabricated into diodes with PIN junction by sandwiching them in between p-type and n-type electrodes. The dark current noise of the two terminal devices is as low as 50 pA/V, several orders of magnitude lower compared to our bulk crystals via ITC. Such crystals are ideal for extracting ultra-low density of carrier with radiation excitations.

ET05.03.27
A Comprehensive Approach to Measuring and Understanding the Electronic Structure of Lead-Halide Perovskite Materials
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Perovskite-based photovoltaics are an emerging solar technology, with device efficiencies exceeding 22% and significant steps are being made towards their commercialisation. In spite of the impressive strides made in device performance and stability, fundamental characterisation of these materials is still severely lacking. Studies of the electronic structure of perovskite materials have resulted in a broad range of values reported for the electronic energy levels and the instability and complex nature of these systems has resulted in a lack of consensus in the electronic properties of these materials. To tackle this ambiguity we have developed a new comprehensive approach to understanding the electronic structure of a perovskite.

In this work the all inorganic perovskite cesium lead bromide (CsPbBr3) is used as a model system. This material was selected as it demonstrates a high stability of both the perovskite material and its non-volatile precursors. We begin by probing the electronic structure of CsBr and PbBr2, we investigate the electronic structure and their contribution to the overall electronic structure of our CsPbBr3. Films prepared with varying concentrations of the precursor materials up to the full perovskite structure have been investigated using X-ray photoemission spectroscopy (UPS) and inverted photoemission spectroscopy (IPES). The surface chemistry of the films, as determined from XPS, and the electronic band gap and valence band character, as determined from UPS and IPES, will be presented. This information is then correlated with morphological and structural data, provided by atomic force microscopy (AFM) and x-ray diffraction (XRD). These techniques enable a full picture of the electronic structure of these systems to be developed and provides a method through which the structure of other perovskite materials can be investigated.

ET05.03.28
Thermodynamic Stability of Halide Perovskites
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Hybrid halide perovskites (HOIPs) have been extensively studied in recent years due to their potential use as light-harvester in photovoltaic devices. While the efficiencies of such devices pose no limitation to commercial applications, the severe lack of stability of the materials remains an important issue to be overcome. Indeed, HOIPs are known to easily degrade under moderate thermal stress(1) or upon oxygen(2) and/or light exposure(3). Notably, recent calorimetric studies even suggested that some HOIPs (MAPbX4 in particular and MAPbBr3 to a minor extent) could be thermodynamically unstable,(3) in contrast, other studies indicate the materials to be intrinsically stable.(4,5) Obviously these questions need to be unambiguously answered. In this contribution, we discuss the underlying thermodynamics of HOIPs, both intrinsically (i.e., with respect to temperature) and extrinsically (against oxygen exposure and/or light). Intrinsically, we find the materials to be stable (albeit, in the case of MAPbI3, only slightly) under standard conditions, and we also can assess the most favorable degradation path upon heating. Extrinsically, our considerations reveal a large tendency towards degradation of HOIPs in the presence of oxygen, especially under real conditions. Notably, light itself can act as a relevant photocatalyst and other mechanisms play a crucial role.

References
Over the past five years, the organolead trihalide perovskites such as CH3NH3PbI3 (MAPbI3) have gained significant research interests with a rapid rise of power conversion efficiency of up to 22%. Integrating MAPbI3 with the two dimensional transition metal dichalcogenides such as MoS2, has the potential of achieving enhanced photosensitivity and broadened absorption bandwidth. In this work, we have integrated MAPbI3 polycrystalline thin film with few-layer MoS2, and demonstrated up to two orders of magnitude enhancement of the photoresponse in the heterostructure compared with the single layer MAPbI3 and MoS2. We mechanically exfoliated few-layer MoS2 flake and transferred it onto the SiO2/Si substrate. The sample was fabricated into 2 point device, on top of which we spincoated uniformly 500 nm MAPbI3 film. Between the two parallel Au electrodes, half of the area contains the MoS2-MAPbI3 hybrid structure, while the other half contains only single layer MAPbI3. We performed high-resolution photocurrent mapping within those two channels, and observed that the MoS2-MAPbI3 region had up to two orders of magnitude higher photocurrent than single layer MAPbI3. The enhancement is attributed to the charge transfer between these two materials due to band alignment, which facilitated photo-carrier separation. The MoS2-MAPbI3 hybrid device showed faster transient photoresponse of 200-300 µs, which makes it promising for constructing high performance photo-detectors.

Enhanced Photoresponse in Hybrid Perovskite Thin Film via Integrating with MoS2

Hua Wu1, Yu Zhang2 and William Yu1; 1Louisiana State University Shreveport, Shreveport, Louisiana, United States; 2Jilin University, Changchun, China.

Perovskite quantum dots are promising optoelectronic materials but are very sensitive to oxygen and water. Here, we report a highly efficient and stable light emitting device (LED) by applying solution-processed Mg-doped ZnO (MZO) nanocrystals (NCs) as an interfacial layer. We investigated the effect of Mg doping on the optical and electronic properties of NCs. We demonstrated that the air stability of perovskite NC film was significantly enhanced because of the decreased oxygen vacancy surface sites of MZO NCs. Incorporation of a MZO layer with favorable electronic energy level to form a suitable band alignment promoted electron injection and enhanced the LED performance. Compared to the device without MZO, the LED showed 3059 cd/m² of luminance, with 1.9 times enhanced current efficiency and 2 times increased external quantum efficiency. In addition, the device with MZO also exhibited better optical and storage stability. This research provides a potential strategy for realizing stable and efficient perovskite LEDs.

Efficient and Stable White LEDs Using Silica-Coated Perovskite Quantum Dots

Chun Sun2, Yu Zhang1 and William Yu1; 1Louisiana State University Shreveport, Shreveport, Louisiana, United States; 2Jilin University, Changchun, China.

Inorganic perovskite QDs (CsPbX3), with narrow size distribution, narrow emission line width, as well as high PL QY without surface shelling, have broad applications. Their emission lights cover the entire visible spectral region and can be easily adjusted. However, their instability and the anion-exchange relaxations of Pr3+ ions. More details of the materials preparation, emission properties of pure and Pr3+ doped CsPbCl3 crystals as well as initial studies for multi-wavelength photonics and nuclear radiation detection will be presented at the conference.

Super-Resolution Infrared Imaging of Mixed Cation Perovskites—Local Compositional Heterogeneities

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Enhanced Photoresponse in Hybrid Perovskite Thin Film via Integrating with MoS2

Luwei Hommerich1, Lanijah Flagg1, Al Amin Kabir1, Althea Bluet2, Sudhir Trivedi1, Clayton S. Yang1 and Feng Jin1; 1Hampton Univ, Hampton, Virginia, United States; 2Chemistry, Geology, and Physics, Elizabeth City State University, Elizabeth City, North Carolina, United States; 3Brimrose Technology Corporation, Sparks Glencoe, Maryland, United States.

We report on the material preparation and emission properties of pure CsPbCl3, and Pr3+ doped CsPbCl3 perovskite crystals for possible applications in multi-wavelength photonics and nuclear radiation detection. The material properties of lead halide perovskites continue to be of great current for optoelectronic applications such as solar cells, light emitting diodes, lasers, and radiation detectors. In this work, we prepared pure and Pr3+ doped CsPbCl3 bulk crystals in an effort to further extend its functionality. The investigated materials were synthesized from purified precursors of PbCl2, CsCl, and PrCl3, followed by melt growth in a vertical Bridgman system. Purification steps included directional freezing and multi-pass unidirectional translation in a zone-melting system. The pure CsPbCl3 crystal exhibited a light yellow color, whereas the Pr: CsPbCl3 crystal was light green indicating the incorporation of Pr3+ ions into the host lattice. Under UV optical pumping (340 nm) the pure CsPbCl3 samples showed bandedge related emission centered at ~410 nm and a broad defect-related emission band extending to ~600 nm. The Pr: CsPbCl3 samples exhibited a bright red emission under resonant intra-4f excitation of Pr3+ ions at 450 nm, with strongest lines peaking at 492 nm, 621 nm, 647 nm, and 732 nm. Furthermore, the Pr: CsPbCl3 sample also exhibited IR emission bands centered at ~1.6 µm, ~2.5 µm and ~4.5 µm under optical pumping at ~1500 nm. The observation of IR emission at room temperature reflects on the low maximum phonon energy of chloride crystals (~250 cm⁻¹), which reduced non-radiative decay though multiphonon relaxations of Pr3+ ions. More details of the materials preparation, emission properties of pure and Pr3+ doped CsPbCl3 crystals as well as initial studies for nuclear radiation detection will be presented at the conference.

Efficient and Stable White LEDs Using Silica-Coated Perovskite Quantum Dots

Chun Sun2, Yu Zhang1 and William Yu1; 1Louisiana State University Shreveport, Shreveport, Louisiana, United States; 2Jilin University, Changchun, China.

Hybrid organic-inorganic lead halide perovskites such as MAPbI3 or FAPbI3 (MA=CH3NH3+ and FA=CH(NH2)2+) and their mixed cation analogues represent one of the most promising alternatives to conventional Si based solar photovoltaics. Intriguing aspects include tunable band gap depending on composition, large optical absorption coefficients, and certified power conversion efficiencies (PCEs) that now exceed 22%. Additionally, composition-
based tunable band gap makes these systems ideal candidates for multi-junction solar cells.

Unfortunately, there has been relatively little work done to explore perovskites compositional cation uniformity. Variation in cation stoichiometry may represent an important limiting factor for these devices as bandgaps—and by immediate extension open circuit voltages—are exquisitely sensitive to local cation composition. Although reports already exist, suggesting cation compositional heterogeneity across perovskite films, this is the first direct study of this phenomenon.

Here, we provide the first direct evidence for intrafilm cation heterogeneities within mixed cation FA,MA$_{1-x}$PbI$_x$ films using a spatially-resolved, super-resolution heated photothermal heterodyne imaging (HR-PHI) technique. We establish that these films exhibit large compositional spatial heterogeneities with cation distributions varying on the order of ~20%, with some areas exceed stoichiometric differences that exceed thrice the expected ideal stoichiometry.

The impact of these cation heterogeneities is further corroborated by emission measurements showing light emission energies differing by over 30meV directly correlated to local stoichiometry. These measurements thus reveal, for the first time, cation stoichiometric heterogeneities and their direct impact on local photovolatic response-determining optical properties of mixed cation perovskites.

**ET05.03.34**

**Highly Efficient and Hysteresis-Less Planar Perovskite Solar Cell with Enhanced Open Circuit Voltage and Stability**

Mohammad Mahdi Tavakoli1, Pankaj Yadav2, Rouhollah Tavakoli3 and Jing Kong1; 1Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Solar, Pandit Deendayal Petroleum University, Gujarat, India; 3Sharif University of Technology, Tehran, Iran (the Islamic Republic of).

Interfacial studies and band alignment engineering on electron transport layer (ETL) play a key role for fabrication of high performance perovskite solar cells (PSCs). Here, we inserted an amorphous layer of SnO$_2$ (a-SnO$_2$) between the TiO$_2$ ETL and the perovskite absorber and studied on the charge transport properties of the device. The double-layer structure of TiO$_2$ compact layer (c-TiO$_2$) and a-SnO$_2$ ETL leads to modification of interface energetics, resulting in improved charge collection and decreased carrier recombination in PSCs. The optimized device based on a-SnO$_2$/c-TiO$_2$ ETL shows a maximum conversion efficiency (PCE) of 21.4% as compared to 19.53% for c-TiO$_2$ based device. Moreover, the modified device demonstrates a maximum open circuit voltage ($V_{oc}$) of 1.223 V with 387 mV loss in potential, which is among the highest value reported for PSCs. In addition, the optimized PSC depicts a negligible hysteresis, and stabilized performance measured under continuous light (AM 1.5G) and UV light illumination. The stability results show that the device on c-TiO$_2$/a-SnO$_2$ has about 91% of its initial PCE value after 500 h light illumination, which is higher than pure c-TiO$_2$ (67%) based devices. Interestingly, using a-SnO$_2$/c-TiO$_2$ ETL the PCE loss was only 10% of initial value under continuous UV light illumination after 50 h, which is higher than that of c-TiO$_2$ based device (28% PCE loss).

**ET05.03.35**

**Prediction of Novel P-Type Transparent Conductors in Layered Double Perovskites—A First-Principles Study**

Jian Xu1,2, Jian-Bo Liu1, Bai-Xin Liu1 and Bing Huang1; 1Tsinghua University, Beijing, China; 2Beijing Computational Science Research Center, Beijing, China.

The development of high-performance transparent conductors (TCs) is critical to various technologies from transparent electronics to solar cells. Whereas n-type TCs have been extensively applied in many electronic devices, their p-type counterparts have not been largely commercialized due to the lack of ideal materials. Combining atomic replacement and first-principles calculations, we have identified 7 stable layered double perovskites, i.e., Cs$_5$Cu$_2$Sb$_2$I$_{12}$-like Cs$_5$M$_2$B$_3$I$_{12}$ compounds as promising p-type TCs with sufficiently large bandgaps, delocalized wavefunction distribution with s-orbital components in valence band maximum (VBM) and the antibonding character of VBM to ensure their optical transparency, light hole effective masses and intrinsic good p-type conductivities, respectively. Taking Cs$_5$GdB$_3$I$_{12}$ as a representative example, we demonstrate that under Cd-poor (Cl-rich) conditions, Cs$_5$CdSb$_2$I$_{12}$ could exhibit excellent p-type conductivity with high hole concentration, contributed by the intrinsic shallow-acceptor Cd$_{\delta}$ with extremely low formation energy. Generally, the other 6 Cs$_5$M$_2$B$_3$I$_{12}$ compounds exhibit similar intrinsic p-type defect properties as Cs$_5$CdSb$_2$I$_{12}$, which could rank them as the top p-type TCs discovered or predicted until now.

**ET05.03.36**

**Direct observation of deep defects in wide bandgap Halide Perovskites**

Igal Levine1, Omar García Vera2, Michael Kulbak1, Carolin Rehermann2, Eva L. Unger2, Gary Hodes1, Isaac Balberg1, David Cahen1 and Thomas Dittrich2; 1Weizmann Inst of Science, Rehovot, Israel; 2Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany; 3The Hebrew University of Jerusalem, Jerusalem, Israel.

Lead Bromide-based perovskites (HaPs) are of interest as parent composition for wide bandgap (> 1.75 eV) absorbers for low-cost solar spectrum splitting to boost solar-to-electrical energy conversion efficiency/area by adding them to c-Si or CIGS PV cells, and for photoelectrochemical solar fuel synthesis. Deep in-gap electronic states in solar cell absorbers serve as recombination centers and are detrimental for the cell’s photovolatic performance, especially the open circuit voltage ($V_{oc}$) of the cell.

However, since several studies showed that the concentration of defects in the HaPs is relatively low (< 10$^{16}$ cm$^{-3}$), there is a general difficulty to observe deep in-gap states by direct optical absorption of sub-band gap photons in the HaPs. Here we use modulated Surface PhotoVoltage (SPV) measurements, a non-destructive contactless technique that relies on direct sub-band gap photon absorption, with exponentially higher sensitivity than photocurrent-based measurements. SPV can show the existence of in-gap states and their relative positions with respect to the band edges both within the bulk semiconductor band gap, as well as at the interfaces of the HaP with the Electron Transport Layer (ETL) or the Hole Transport Layer (HTL).

For the first time, we reveal that three different, deep, defect levels exist in the bulk of the mix- Cation Lead Tribromide layers. Two of the levels are close to midgap, and the third lies ~0.8 eV below the Conduction Band Maximum (CBM). We also find that aging in inert atmosphere, as well as light soaking, increases the defect concentration. Furthermore, by performing photoconductivity measurements over a wide excitation intensity range, we show that under steady-state 1-sun equivalent conditions, these sub-band gap defect levels play an active role as non-radiative recombination centers.

**ET05.03.37**

**Composition Engineering and Microspectroscopic Study for Efficient and Spectrally Stable Mixed Halide Perovskite LEDs**

Yongzheng Jia, Yuwei Guo, Yang Zhou and Ni Zhao; EE, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Quickly following the development of perovskite solar cells, the field of perovskite light-emitting diodes (LEDs) has proceeded rapidly, with some devices already achieving comparable efficiencies with those of the state-of-the-art organic LEDs. Perovskite LEDs offer tunable emission wavelength from visible to near-infrared, however, in certain spectral range the device performance is highly unstable. Taking red-emitting perovskite LEDs as an example, since the devices often rely on a mixed bromide-iodide perovskite for light emission, the typical light-induced phase segregation behavior of the material system results in a rapid red-shift of the electroluminescence (EL) peak, leading to a color change of the LEDs. In this presentation, we will introduce our recent endeavors on composition engineering and optical microspectroscopy to address the aforementioned stability problem of perovskite LEDs. We show that by simultaneously introducing lead thiocyanate and organoiodine additives in the perovskite precursors one can obtain a stable perovskite phase with high photoluminescence quantum yield (PLQY). The corresponding LEDs exhibit stable spectral emission and good performances (e.g., irradiance of 400 W/sm$^2$).
The metal halide perovskite solar cells (PSCs) have become one of the most popular types of photovoltaic devices in past 6 years. High power-conversion-efficiency (PCE), panchromatic light absorptions and long carrier diffusion length, etc, make the PSCs significantly competitive among the thin film solar cells. However, optimal function and performance of the PSCs usually require high quality of a perovskite film with full coverage, low roughness, big grain size and proper thickness, etc. Numerous methods have been applied to make high quality perovskite film, among which, the solution-based spin coating is one of the most vastly used methods. Although different groups have succeeded in making perovskite film using the spin coating, specific conditions such as solvent type, thermal treatment etc., varies largely. Lack of rational comparisons and instructive guidance on the deposition condition selection result in huge difficulty in performing repeatable experiments. Herein, we compare the effect of solvents, co-solvents and their ratios on the quality of the perovskite thin films. DMF and/or GBL are used as major solvents, while DMSO is applied as the co-solvent. Several ratios of DMF/GBL to DMSO from 10:0, 9:1 to 7:3 have been tried to prepare the perovskite precursor solutions. Interestingly, we observe significant differences on crystallinity, morphology and thickness of the thin film made by different types and combination of solvents. For instance, 1) From the XRD data, perovskite deposited from DMF-based solution exhibits 10 times stronger crystallinity as compared with samples made from GBL. 2) SEM images indicate that DMF-based solution guarantees compact and 2 times thicker films than the GBL ones, while the surface of DMF made layer shows much higher roughness. 3) Reducing the amount of the DMSO in the solution can promote the smoothness of the surface but result in the decrease of the film thickness. 4) Crystals with smaller grain size are observed in samples made from solution without DMSO, while excessive of DMSO content leads to vacancies inside the films. 5) Films deposited from the combined solvents of 90% DMF and 10% DMSO presents best compactness, thickness, smoothness and crystallinity among all other solvent combinations, showing 1.5-2 times longer charge carrier lifetime and superb PCE with the best device exceeding 17%. We attribute the better quality of DMF deposited layers to higher PbI$_2$ solubility and lower boiling point of the DMF, as compared with GBL. The addition of DMSO slows down the crystal growth rate of perovskite by forming MAI-DMSO-PbI$_2$ intermediate, guaranteeing larger crystal grain size. While excessive DMSO, which does not participate in the formation of the intermediates, remains in the supersaturated film (before annealing) and causes rupture and vacancies in the film during the vigorous annealing process. (This work was supported by the Morin Foundation Trust and the NSF, Inspire program #1344267)

**ET05.03.38**  
Highly Luminescent 0D Organic Metal Halide Hybrids with Tunable Colors  
Chenkun Zhou$^1$, Haoran Lin$^1$, Michael Worku$^1$, Jennifer Neul$^1$, Yan Zhou$^1$, Yu Tian$^1$, Peter I. Djurovich$^2$, Theo Siegrist$^3$ and Biwu Ma$^1$  
$^1$Florida State University, Tallahassee, Florida, United States; $^2$University of Southern California, Los Angeles, California, United States; $^3$FAMU-FSU College of Engineering, Tallahassee, Florida, United States.

Organic-inorganic metal halide hybrids, consisting of a great variety of inorganic metal halide anions and organic cations, are an emerging class of functional crystalline materials with exceptional structural tunability. By choosing appropriate organic and inorganic components, the crystallographic structures can be finely engineered with the inorganic metal halides forming three-dimensional (3D) networks, two-dimensional (2D) planar or corrugated layers, one-dimensional (1D) chains or tubes, and zero-dimensional (0D) structures. The structural versatility of this class of materials suggests there is a vast parameter space to explore novel crystal structures exhibiting properties obeying non-obvious trends. In this talk, I will present our recent efforts in developing and studying new classes of 0D metal halide hybrids. By choosing appropriate organic and inorganic components, the emitting species in 0D structure can be tuned from MX$_2$ octahedra to MX$_2$ pyramids, MX$_3$ seeaw structure, and metal halide clusters. Due to the structural reorganization and efficient intersystem crossing on the excited states, highly luminescent broadband emissions with large Stokes shift have been achieved for these 0D metal halide hybrids. Our findings show the molecular nature of small metal halide species in the 0D structure and allow us to relate the emission from either structure reorganization or localized excitons in metal halides to molecular phosphorescence. The application of these 0D materials as down converter in optically pumped white light emitting diodes will also be discussed.

**ET05.03.39**  
Solvent Effects on the Thin-Film Quality and Photovoltaic Performance of Metal Halide Perovskites  
Yuchen Zhou$^1$, Yifan Yin$^1$, Chang-Yong Nam$^2$ and Miriam Rafailovich$^1$  
$^1$Stony Brook University, Stony Brook, New York, United States; $^2$Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States.

The metal halide perovskite solar cells (PSCs) has become one of the most popular types of photovoltaic devices in past 6 years. High power-conversion-efficiency (PCE), panchromatic light absorptions and long carrier diffusion length, etc, makes the PSCs significantly competitive among the thin film solar cells. However, optimal function and performance of the PSCs usually require high quality of a perovskite film with full coverage, low roughness, big grain size and proper thickness, etc. Numerous methods have been applied to make high quality perovskite film, among which, the solution-based spin coating is one of the most vastly used methods. Although different groups have succeeded in making perovskite film using the spin coating, specific conditions such as solvent type, thermal treatment etc., varies largely. Lack of rational comparisons and instructive guidance on the deposition condition selection result in huge difficulty in performing repeatable experiments. Herein, we compare the effect of solvents, co-solvents and their ratios on the quality of the perovskite thin films. DMF and/or GBL are used as major solvents, while DMSO is applied as the co-solvent. Several ratios of DMF/GBL to DMSO from 10:0, 9:1 to 7:3 have been tried to prepare the perovskite precursor solutions. Interestingly, we observe significant differences on crystallinity, morphology and thickness of the thin film made by different types and combination of solvents. For instance, 1) From the XRD data, perovskite deposited from DMF-based solution exhibits 10 times stronger crystallinity as compared with samples made from GBL. 2) SEM images indicate that DMF based solution guarantees compact and 2 times thicker films than the GBL ones, while the surface of DMF made layer shows much higher roughness. 3) Reducing the amount of the DMSO in the solution can promote the smoothness of the surface but result in the decrease of the film thickness. 4) Crystals with smaller grain size are observed in samples made from solution without DMSO, while excessive of DMSO content leads to vacancies inside the films. 5) Films deposited from the combined solvents of 90% DMF and 10% DMSO presents best compactness, thickness, smoothness and crystallinity among all other solvent combinations, showing 1.5-2 times longer charge carrier lifetime and superb PCE with the best device exceeding 17%. We attribute the better quality of DMF deposited layers to higher PbI$_2$ solubility and lower boiling point of the DMF, as compared with GBL. The addition of DMSO slows down the crystal growth rate of perovskite by forming MAI-DMSO-PbI$_2$ intermediate, guaranteeing larger crystal grain size. While excessive DMSO, which does not participate in the formation of the intermediates, remains in the supersaturated film (before annealing) and causes rupture and vacancies in the film during the vigorous annealing process. (This work was supported by the Morin Foundation Trust and the NSF, Inspire program #1344267)

**ET05.03.40**  
Effect of Chromium Doping on the Electronic Structure of CH$_3$NH$_3$PbI$_3$ Perovskite  
Perovskite Perla Wahnon-Benarroch$^1$, Gregorio Garcia$^1$, Pablo Palacios$^1$, Jose Carlos Conesa$^2$, Ana Lilian Montero$^2$ and Eduardo Menendez-Proupin$^2$  
$^1$Universitat Politècnica de Madrid, Madrid, Spain; $^2$Consejo Superior de Investigaciones Científicas, Madrid, Spain; $^3$Universidad de Chile, Santiago, Chile.

Organic-inorganic lead halide perovskites (mainly CH$_3$NH$_3$PbI$_3$) are being extensively studied because their excellent photovoltaic properties, such as suitable bandgap, high optical absorption and long carrier lifetime. To explain the large recombination time, the hypothesis that the formation of ferroelectric domains can separate the diffusion pathways of electrons and holes, has been proposed. We have found that a two-dimensional hole confinement in CH$_3$NH$_3$PbI$_3$ is possible under room temperature conditions. In this work, we explore the possibility of increasing their photovoltaic efficiency through additional sub-bandgap absorption. This would result in the creation of extra electron-hole pairs and in an increase in photocurrent without a decrease in open-circuit voltage. We assess the formation of a new band in the gap as well as its effect on the absorption features of hybrid halide perovskites CH$_3$NH$_3$PbI$_3$ (MAPI). This approach has been widely studied to improve the efficiency of common semiconductors with photovoltaic performance such as GaP, CuInS$_2$, thiospinels, SnS$_2$ or Si. To better understand the morphology-performance correlation, we apply charge-modulation microspectroscopy (CMM) to investigate the electric-field inhomogeneity in the perovskite film, the impact of electron- (or hole-) transport layer on the LED EL properties, as well as the spatially resolved degradation processes in the electrode-covered and -uncovered regions. The findings provide some guidelines to the design of perovskite LED structures.

G. Garcia, P. Palacios, et al. Scientific Reports, 2018, 8,2511

**ET05.03.41**  
Monitoring Nonradiative Charge Carrier Recombination and Extending the Excited State Lifetimes in Methylammonium Lead Bromide Perovskite Nanocrystals  
Christopher McClussee$^1$, David Stewart$^1$, Todd Grussenmeyer$^1$, Thomas M. Cooper$^1$ and Joy Haley$^1$  
Air Force Research Laboratory, Dayton, Ohio; United States; General Dynamics Information Technology, Dayton, Ohio, United States.
Lead halide perovskites have applications in the fields of photovoltaics, light emitting diodes, and lasers. Their success results from their high absorption coefficients, low exciton binding energy, long charge carrier diffusion lengths, and high photoluminescence quantum yields. In order to optimize these devices to their full potential, it is important to understand their fundamental photophysical properties and how processing conditions affect their optical and electronic properties. Currently in the literature, the majority of time-resolved optical studies on perovskite nanocrystals utilize time-resolved photoluminescence to determine the excited state lifetimes. However, the nonradiative recombination processes should be further investigated due to the fact that they can have drastically different charge carrier recombination rates. Here, steady state and time-resolved optical spectroscopy is used to study the photophysical properties of hybrid organic-inorganic methylammonium lead bromide nanocrystals. Time-resolved spectroscopy measurements show that the band edge bleach decay dynamics are longer compared to the photoluminescence decay. These results indicate that dark carrier recombination is the primary mechanism leading to the long lived excited state lifetime of perovskite nanocrystals. Additionally, the effect of the precursor starting material purity on the excited state lifetimes is investigated.

**ET05.03.42**
**Mapping the Inter-Diffusion of A-Site Cations in Metal Halide Perovskites**
Sarthak Jariwala, Irika Sinha, Kathryn N. Guye and David S. Ginger; University of Washington, Seattle, Washington, United States.

We measure the inter-diffusion of methylammonium (MA) and formamidinium (FA) cations using lateral heterojunctions formed between MAPbI3 and FAPbI3. We confirm the creation of the gradient using UV-Vis and steady-state photoluminescence (PL) measurements demonstrating a bandgap of ~1.58 eV for the MAPbI3 portion and ~1.49 eV for the FAPbI3 portion of the film. We confirm that there is no change in the film morphology and crystallinity as evidenced by SEM and XRD, respectively. Using PL line scans across the lateral gradient, we image the inter-diffusion of MA and FA as a function of position and time. Using Fick’s Diffusion equations to fit the PL line scans, we determine the MA-FA inter-diffusion coefficient to be ~2x10^-8 cm^2s^{-1}. We also monitor the inter-diffusion of cations spatially and temporally using in-situ widefield and confocal PL imaging to correlate cation motion with grain morphology. We observe the regions with low intensity undergo a faster exchange from MAPbI3 to FAPbI3. Furthermore, from confocal scans, we observe regional variations in MA-FA exchange. We show that regions with low PL intensity demonstrate a higher final FA concentration than regions with high PL intensity. This shows that the MA-FA exchange is faster in regions with higher defect-concentration suggesting a connection between non-radiative decay and ion exchange.

**SESSION ET05.04: Photophysics, Carrier Dynamics and Device Mechanisms**
Session Chairs: Samuel Stranks and Yanfa Yan
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room Ballroom B

**8:00 AM ET05.04.01**
**Are Charge-Carrier Recombination Processes in Halide Perovskites Unique?**
Dane W. deQuillettes1, 2, Kyle Frohna1, David Emiri1, Thomas Kirchherr2 and Samuel D. Stranks3; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Chemistry, University of Washington, Seattle, Washington, United States; 3University of Cambridge, Cambridge, United Kingdom; 4The University of New Mexico, Albuquerque, New Mexico, United States; 5Universität Duisburg-Essen, Duisberg, Germany.

The success of halide perovskites in a host of optoelectronic applications is often attributed to long carrier lifetimes despite a non-negligible population of defects. Although this “slow” recombination has been proposed to be a key enabling property of perovskites, the photophysics which govern the long lifetimes are still poorly understood. In fact, some authors have argued that the experimentally measured radiative recombination rate does not differ from what is theoretically expected based on the well-known reciprocity between absorption and emission rates. Contrarily, others have argued that recombination in perovskites is unique and may be impeded by benign trap states, polaron formation, the indirect nature of the bandgap, and photon recycling. Here, I will discuss whether recombination in perovskites is indeed unique by first placing the experimentally measured recombination rates within the context of classic semiconductor theory and next, extending this analysis by performing numerical simulations to evaluate how the other proposed mechanisms could further affect charge carrier kinetics. I will highlight the interdependence of these processes and suggest future experiments to decouple their relative contributions. A complete understanding of the recombination processes in these fascinating semiconductors would provide guidelines for designing new materials with favorable optoelectronic properties.

**8:15 AM ET05.04.02**
**Time-Resolved Imaging of Charge Carrier Diffusion in Hybrid Organic-Inorganic Perovskite Thin Films**
Aravindan Sridharan1, Nakita K. Noel2, Hyeon Hwang1, Soroush Hafezian1, Barry P. Rand2 and Stéphane Kéna-Cohen1; 1Engineering Physics, Polytechnique Montréal, Montreal, Quebec, Canada; 2Electrical Engineering, Princeton University, Princeton, New Jersey, United States.

Hybrid inorganic-organic perovskites, due to their optoelectronic properties leading to very high-power conversion efficiencies, have shown great potential as absorbers in solar cells. Long-range diffusion of charge carriers was shown to be an important property contributing to a higher extraction of the photogenerated carriers. Here, we develop a streak-camera based time-resolved imaging technique and use it to directly probe carrier diffusion and recombination kinetics in hybrid perovskites. We study MAPbI3 obtained via different fabrication routes, FAPbI3, FA0.85MA0.15Pb(I0.85Br0.15)3, and MAPbBr3. Small diffusion coefficients of ~0.9 × 10^-5 and ~2.1 × 10^-5 cm^2s^{-1} are found in the films showing the highest device efficiencies, i.e., in FAPbI3, FA0.85MA0.15Pb(I0.85Br0.15)3, and MAPbBr3 (acetonitrile processed), respectively. In contrast, much higher values are found in MAPbI3 and FAPbI3 films, i.e. 4.9 × 10^-3 cm^2s^{-1} and 2.7 × 10^-3 cm^2s^{-1}, respectively. We find that in addition to diffusion, the interplay between the monomolecular and bimolecular recombination processes is a critical factor determining device efficiency.

**8:30 AM ET05.04.03**
**Fundamental Mechanisms of Light Conversion in Metal Halide Perovskites for Photovoltaics**
Laura Herz; University of Oxford, Oxford, United Kingdom.

Organic-inorganic metal halide perovskites have emerged as attractive materials for solar cells with power-conversion efficiencies now exceeding 21%. We discuss the fundamental photophysical processes that have enabled these materials to be such efficient light-harvesters and charge collectors.

As photovoltaic power conversion efficiencies of single-junction cells approach the Shockley-Queisser limit, the recombination and mobility of charge-carriers will be limited only by intrinsic properties. We demonstrate that at the intrinsic limit, the mobility of charge-carriers is predominantly governed by...
interaction of carriers with optical vibrations of the lead halide lattice (Fröhlich interaction)\(^{(3)}\). Therefore, predictions of maximum attainable mobilities can be made from easily accessible parameters, such as LO phonon frequencies and limits of the dielectric function\(^{(2)}\).

In the absence of trap-mediated charge recombination, bi-molecular (band-to-band) recombination will dominate the charge-carrier losses near the Shockley-Queisser limit. We show that in methylammonium lead triiodide perovskite, such processes can be fully explained as the inverse of absorption, and exhibit a dynamic that is heavily influences by photon reabsorption inside the material\(^{(4)}\).

Finally, we examine the prospect of such highly performing hybrid lead iodide perovskites in solar concentrator environments.\(^{(5)}\) We demonstrate that in the absence of degradation, perovskite solar cells can fundamentally exhibit appreciably higher energy-conversion efficiencies under solar concentration, where they should be able to exceed the Shockley-Queisser limit and exhibit strongly elevated open-circuit voltages.

References


9:00 AM ET05.04.04 Impact of the Rashba Effect on Radiative Recombination in Hybrid Perovskites Xie Zhang, Jimmy-Xuan Shen, Wennie Wang and Chris G. Van de Walle; University of California, Santa Barbara, California, United States.

Hybrid perovskites exhibit pronounced momentum splitting at band edges due to a strong Rashba spin-orbit coupling effect. This effect was invoked by a number of groups to explain the high efficiency of hybrid perovskite solar cells. It was argued that the Rashba-induced splitting effectively suppresses the radiative recombination by mismatched spins and momenta between photoexcited electrons and holes. In the present study, we perform first-principles calculations to explicitly examine the impact of the Rashba effect on the radiative recombination coefficient in the archetype hybrid perovskite, CH₃NH₂PbI₄. We demonstrate that the band extrema have consistent spin orientation and the momentum mismatch affects the radiative recombination coefficient by less than a factor of two. The computed radiative recombination coefficients are as high as in typical direct-gap semiconductors. Our insights establish a solid basis for accurate modeling of hybrid perovskites.

9:15 AM ET05.04.05 Impact of Layer Thickness on the Charge Carrier and Spin Dynamics in 2D Layered Perovskite Single Crystals Haipeng Lu, Xihan Chen and Matthew C. Beard; National Renewable Energy Laboratory, Golden, Colorado, United States.

Recently, 2-dimensional (2D) Ruddlesden-Popper lead-halide based perovskite layered systems are attracting attention. Compared to their 3D counterpart, 2D systems offer greater tunability and stability, making them candidates for high-performance optoelectronic applications. Here we report the charge carrier recombination rate and spin depolarization times in single crystals of 2D perovskites PEA₂PbI₄ (MA₂PbI₄)₁₋ₓ (PEA, phenethylammonium; MA, methylammonium; n = 1, 2, 3, 4). Layer thickness dependent charge carrier recombination rates were observed with the fastest rates for n = 1 due to the large exciton binding energy. Interestingly the slowest recombination times occurred for the n = 2 sample and not n = 4. Room temperature spin-decoherence times also show a nonmonotonic layer thickness dependence with an increasing spin-coherence lifetime with increasing layer thickness from n = 1 to n = 4, followed by a decrease in lifetime from n = 4 to n → ∞. The longest decoherence time of ~7 ps is observed in the n = 4 sample. Our results are consistent with two contributions; Rashba-splitting increases the spin-coherence time going from the n = ∞ to the layered systems, while phonon-scattering which increases for smaller layers decreases the spin-coherence time. The interplay between these two factors contributes to the layer thickness dependent spin-coherence lifetimes. To correlate we monitored the LO and TO phonon frequency and phonon linewidth. For thinner layers the phonon frequencies decrease and broaden substantially indicating a large electron-phonon coupling.

9:30 AM ET05.04.06 Charge Carrier Dynamics in Metal Halide Perovskite Solar Cells Change after Exposure to Humidity and Light Esma Ugur, Jafar I. Khan, Erkki Alarousu, Sandra P. Gonzalez-Lopez and Frédéric Laquai; King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

In a very short time span, the power conversion efficiency (PCE) of metal halide perovskite solar cells (PSCs) has reached 23%, a massive improvement for solution-processed photovoltaic devices. Towards this end, both surface and bulk recombination of photogenerated charge carriers in the perovskite absorber layer are the major efficiency-limiting factors. [1] In this respect, controlling the growth and crystallization of the perovskite thin film is crucial for the performance of the perovskite solar cells as the crystal growth dynamics are very susceptible to the processing conditions [2]. Interestingly, some studies report a beneficial effect from water inclusion during processing, while others claim an adverse effect. Moreover, the effect of humidity and light exposure on the performance of PSCs is still debated. In this study, we fabricated, using a two-step protocol, MAPbI₃ perovskite solar cells with SnO₂ electron transport layers to study how the device performance and photophysics change upon exposure to humidity and light. Reference devices, not exposed to humidity and light, exhibit 18.4 % PCE with 22.5 mA/cm² short-circuit current density (Jsc) and 1.12 V open circuit voltage (Voc). After exposing the perovskite absorber layer to 55% relative humidity under 1-sun illumination prior to completing the device fabrication, a reduction in Voc to 1.09 V was observed. We study the influence of excess lead iodide (PbI₂), which is commonly believed to be passivating the PSCs, on the humidity resistance of MAPbI₃ devices. While the Voc value of samples with excess-PbI₂ was lowered to 1.10V, we did not observe any change in Jsc. Since Voc losses can be attributed to non-radiative recombination, we performed time-resolved photoluminescence (TR-PL) spectroscopy before and after humid air exposure of perovskite thin films under 1-sun illumination. We will discuss in detail how the exposure to humid air under illumination alters the surface structure of the perovskite samples, affects the device performance, and the photophysical processes.

References


9:45 AM BREAK

10:15 AM ET05.04.07 Ferroelectric Large Polarons in Lead Halide Perovskites Xiaoyang Zhu; Columbia University, New York, New York, United States.
Loss Mechanisms in Perovskite Solar Cells—Initially and During Aging

Solar cells based on lead halide perovskites have recently emerged showing a tremendous increase of power-conversion efficiency which exceeded 22%. In this contribution, the device physics of perovskite solar cells is addressed. The focus is on recombination of charge carriers because this process is ultimately limiting the efficiency. Furthermore, the performance and changes thereof during light-soaking and operation under real weather conditions are addressed.

The origin of the open-circuit voltage is discussed based on the reciprocity relation between electroluminescence and photovoltaic quantum efficiency.¹ Sharp absorption onset and high radiative recombination yield due to an extraordinary defect tolerance are identified as reasons for the outstanding optoelectronic properties of perovskites. Furthermore, the role of defect and surface recombination are addressed by employing a detailed analysis of the diode ideality factor.² Upon deliberately introducing defects in a controlled way it is found that the defect tolerance does not span to any kind of extrinsic defect.

The current-voltage curve of perovskite solar cells yields different results dependent on the initial voltage and scan rate of the voltage sweep. The resulting hysteresis is related to recombination as well.³ These results are explained based on the mixed ionic and electronic conductivity of the material, where displaced ions change interface and defect recombination rates. Reversible effects are observed on timescales of hours and their origins distinguished from irreversible degradation.⁴ The interplay of all these processes is analyzed for long-term operation under real weather conditions, where a better low-light performance and a low temperature coefficient result in relatively higher energy yields compared to a silicon solar cell.

An outlook is given on strategies aiming for a further improvement of open-circuit voltage and performance of perovskite solar cells toward their thermodynamic limit.

References

Imaging the Inhomogeneous Trap State Distribution in Hybrid Organic-Inorganic Perovskite Films

Hybrid organic-inorganic perovskite semiconductors have recently emerged as high-performance thin-film photovoltaic materials. Their combination of good optoelectronic properties and low-cost synthesis processes has led to an unprecedented rate of development in perovskite-based solar cells over several years. Despite this development, however, there are still ongoing efforts to reduce unwanted non-radiative carrier loss and further push solar conversion efficiencies towards theoretical limits. One of the phenomenological observations highlighting the efficiency limits is the non-uniform radiative emission seen in photoluminescence (PL) microscopy, suggesting that there is an underlying nanoscale variation in the carrier trapping centers in solution-processed perovskite films.

Here, we utilize time-resolved photoemission electron microscopy (TR-PEEM) to view directly the nanoscale electronic variation and its effect on photo-excited carriers in mixed cation perovskite films. We investigate regions with different PL efficiency and find an increased number of nanoscale trap centers in low PL efficiency regions. We show that these traps are due to occupied mid-gap states and probe the corresponding ultrafast hole trapping dynamics at these nanoscale locations. Our work gives a direct view at the nanoscale distribution of trap centers in perovskite materials and their connection to macroscopic carrier recombination.

Recombination Routes of the Free Carriers in Perovskite Solar Cells Revealed by Intensity-Modulated Photovoltage Spectroscopy

In intensity-modulated photovoltage spectroscopy (IMVS) and impedance spectroscopy (IS) experiments of perovskite solar cells (PSCs), two features with different power dependencies are observed to correspond to two relaxation routes. The relaxation rate of the slower feature is independent of light power while that of the faster one is proportional to the light power. Similar power dependence is observed in PSCs with various hole transport layers. Apparently, understanding the slower process will be helpful in optimizing the electric hysteresis in PSCs. In addition, because previous report assigns the faster process to the recombination of free carriers, understanding the faster feature will be helpful in minimizing the photocarrier loss in PSCs. We notice that the recombination mechanisms involving only free carriers (e.g., band-to-band recombination) yield sublinear power dependence. Therefore at least potential carrier species should be considered to explain the linear power dependence of the faster feature. Consequently, the next question is what is the second carrier species other than free carriers is. We think it could be either accumulated carriers involved in the surface polarization model or the mobile ions/vacancies. In order to convincingly assign it, various photoelectric measurements are performed to provide additional information to these carriers. Our results indicate that these carriers should 1) be photogenerated with fixed lifetime (regardless of light power) so that its number is proportional to light power, 2) readily migrate along the electrode/perovskite surface so that it could uniformly distribute the device area (0.26 cm²), 3) be thermally activated before it could recombine with the free carriers, 4) be directly relevant to the slower IMVS or IS feature.

Recombination Routes of the Free Carriers in Perovskite Solar Cells Revealed by Intensity-Modulated Photovoltage Spectroscopy

Xiaqing Chen, Yasuhiro Shirai, Masatoshi Yanagida and Kenjiro Miyano; National Institute for Materials Science, Tsukuba, Japan.

Recombination Routes of the Free Carriers in Perovskite Solar Cells Revealed by Intensity-Modulated Photovoltage Spectroscopy

Xiaqing Chen, Yasuhiro Shirai, Masatoshi Yanagida and Kenjiro Miyano; National Institute for Materials Science, Tsukuba, Japan.

Recombination Routes of the Free Carriers in Perovskite Solar Cells Revealed by Intensity-Modulated Photovoltage Spectroscopy

Xiaqing Chen, Yasuhiro Shirai, Masatoshi Yanagida and Kenjiro Miyano; National Institute for Materials Science, Tsukuba, Japan.
Metal-halide perovskites have demonstrated exceptional optoelectronic properties for next generation photovoltaics and light-emitting diodes. Recently, cation substitution has been reported to generate luminescence very efficiently, yet the underlying photo-physics are poorly understood. Here, we study the origin of this increased brightness by combining transient absorption and photoluminescence (PL) spectroscopy to track charge carrier dynamics in perovskite thin films. Unexpectedly, we find the recombination behavior to change from the previously-reported second to a first order regime within tens of nanoseconds after excitation, in line with fluence-dependent PLQE measurements. In temperature-dependent PL we find a redshift of the luminescence with decreasing temperature, directly mapping localized shallow traps. Supported by DFT calculations and transistor measurements we propose that energetic disorder in the distribution of electronic states leads to spatial accumulation of charges, creating n- and p-type doped regions, explaining the PLQE observations. Our results indicate that strong luminescence can be achieved in mixed-cation perovskites even at low carrier densities and thereby provides a roadmap for highly efficient LEDs.

References

1:30 PM *ET05.05.01/ET04.05.01
Hybrid Halide Perovskite Semiconductors—An Historical Perspective David B. Mitzi; Duke University, Durham, North Carolina, United States.

Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable structures/band gaps, relatively benign defects and grain boundaries, and facile processing for systems based on Group 14 metals (e.g., Ge, Sn and Pb). Most recently, these materials have enabled unprecedented rapid improvement in performance within single junction photovoltaic (PV) devices, from an initial demonstration in 2009 [2] to levels with >20% power conversion efficiency and open circuit voltages >1V [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite semiconductors, including discussion of crystal structure flexibility, semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures [4,5]. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.

References

2:00 PM *ET05.05.02/ET04.05.02
Photovoltaics of Halide Perovskites and Perspectives of Extensive Applications from the Ground to the Universe Tsutomu Miyasaka; Toin University of Yokohama, Yokohama, Japan.

Lead halide perovskite absorbers have achieved high photovoltaic performance exceeding the efficiency of CIGS and CdTe and their long term stability against heat, moisture, and light are being improved by compositional engineering of perovskite and surrounding carrier transport materials. For industrial applications, thermal stability of perovskites and carrier transport materials is a critical issue in comparison with thermally highly strong inorganic solar cell (Si, CdTe, etc.). Metal oxide electron transport layers (ETLs) generally have advantage in higher thermal stability than organic ETLs. We have been working with TiO2 ETL-based multi-cation perovskite cells, which yielded efficiency over 21% by ambient air solution processes. Light intensity dependence of Voc shows ideality factor low enough (n<1.4) for the perovskite solar cell to work as a high voltage power source even under weak light. Such merit meets a requirement in solar cell application to space satellite missions, which needs high photovoltaic performance even under very weak sunlight (Mars and Jupiter). We have examined the durability of perovskite solar cells which have thermally stable compositions comprising FA-based perovskites, TiO2 ETL, and P3HT as hole transport layer (HTL). These cells exhibit good stability against thermal impact between temperature range near -80°C and +100°C. We also confirmed very poor thermal stability of spiro-OMeTAD as a reference HTL. On exposure to high energy electron and proton radiations as accelerated conditions simulating long term space irradiations, the perovskite cells demonstrated high stability and tolerance, which are superior to those of Si and GaAs solar cells. Space applications also require fabrication of lightweight flexible devices. Thin film substrate-based perovskite solar cells were fabricated by low-temperature multilayer coating methods using amorphous TiO2 as ETL, which yield efficiency up to 18%. Future perspectives of industrialization of perovskite photovoltaic devices will be discussed focusing on the durable composition of perovskite devices and advantage of lightweight thin film device.

References
Compositional Engineering for Efficient and Durable Perovskite Solar Cells

Anders Hagfeldt;
Laboratory of Photomolecular Science, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland.

3:30 PM *ET05.05.04/ET04.05.04

3:30 PM

Compositional Engineering for Efficient and Durable Perovskite Solar Cells

Anders Hagfeldt;
Laboratory of Photomolecular Science, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 20% with a mixed composition of iodide/bromide and methyl ammonium/formamidinium [1]. For cells larger than 1 cm² we have obtained 19.6% [2], replacing the anti-solvent step in the perovskite film formation with a vacuum flash treatment. With the use of SnO2 compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20% [3]. The cation mixing strategy has been developed further by including the Cs in a so-called ‘triple cation’ composition, i.e. Cs/FA/MA as well as Rb in a quadruple cation mixture. Larger grains grown in a monolithic manner are observed and for example reproducibility and device stability are improved [4]. At the meeting we will discuss our follow up works [5] and present our champion data; up to 22% efficiency with an external electroluminescence of 4%, and an outstanding open-circuit voltage of 1.24 V at a band gap of 1.63 eV entailing one of the smallest loss-in-potential of 0.39 V ever measured for any solar cell material. Furthermore, we will report promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (during which 95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests [6].

Keywords: Perovskite, composition, stability

References

[1] Bi et al., Science Advance, DOI: 10.1126/sciadv.1501170

4:00 PM *ET05.05.05/ET04.05.05

Perovskite Solar Cells—The Path to a Printable Terawatt-Scale Technology

Kai Zhu; National Renewable Energy Laboratory, Golden, Colorado, United States.

Perovskite solar cells (PSCs) have become a competitive photovoltaic (PV) technology with rapid progress of efficiencies reaching to about 23%. Uniquely, PSCs have the highest efficiencies when they are solution processed, so one can envision solar cells printed in a similar manner and scale as newspapers. In addition, the band gap tunability through perovskite composition engineering can enable high-efficiency multijunction devices, including perovskite/perovskite, perovskite/silicon, or perovskite/thin-film absorber (e.g., CIGS). Thus, PSCs are suited to helping address the challenge of terawatt-scale, PV-based electricity production that can power the future world. In this talk, I will discuss our recent progress in two areas: (1) scalable fabrication of high-efficiency, large-area perovskite solar cells and modules; (2) development of perovskite-based tandem devices. I will discuss our recent studies toward better control of film formation across the device stack at large scales by improving the precursor chemistry to better match the processing methods. The precursor chemistry and growth conditions affect significantly the physical and optoelectronic properties of perovskites. The challenges associated with perovskite solar module fabrication will be discussed. I will show the impact of interconnections on the performance of perovskite solar modules fabricated by scalable depositions. Toward perovskite-based tandem device development, I will discuss our recent effort on improving the optoelectronic properties of wide-bandgap as well as low-bandgap perovskite absorbers through solution chemistry engineering. Challenges and progress on perovskite-based tandem devices will also be discussed. These results demonstrate a promising path towards commercialization of the perovskite photovoltaic technology.

4:30 PM DISCUSSION PANEL: UNSOLVED PEROVSKITE PROBLEMS—OPPORTUNITIES AND CHALLENGES - DISCUSSION

LEADER: IVÁN MORA-SERÓ

SESSION ET05.06: Poster Session II: Fundamentals of Halide Perovskite Optoelectronics

Session Chair: Philip Schulz
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET05.06.01

Photobleaching and Recovery of Photoluminescence of CsPbBr3 Perovskite Quantum Dot

Yoshiki Iso, Koji Kidokoro and Tetsuhiko Isobe; Keio Univ, Yokohama, Japan.

CsPbX₃ (X = Cl, Br, I) perovskite quantum dots (QDs) have attracted many attentions because of their excellent photoluminescence (PL) properties such as high quantum yields, narrow PL peak widths, and emission color tunability by elemental composition of the halide ions. CsPbBr₃ QD, which exhibit highly-pure green emission under blue and UV light irradiation, is a good candidate for applications to wide-color gamut displays. However, photodegradation of the CsPbBr₃ QD under excitation is a significant problem to be solved for their practical use. Herein, we found recovery of photodegraded CsPbBr₃ QD after continuous blue light excitation. In this work, the photobleaching and recovery phenomena of the CsPbBr₃ QD are investigated by evaluation of their optical properties. CsPbBr₃ QD was synthesized by a conventional hot-injection method. Cs₂CO₃ was added into a mixture of 1-octadecene and oleic acid. The mixture was...
Minimizing Non-Radiative Losses Through Rational Defect Passivation for High Performance Perovskite Light-Emitting Diodes

ET05.06.04

Understanding Grain Boundary Effects in Methyrammonium Lead Bromide Films Using Electron Backscatter Diffraction (EBSD) Gede Adhyaksa1, Sarah Brittan1, Haralds Abolins2, Andries Loft3, Xueying Li4, Joel D. Keeler5, Yanqi Luo6, Teodor Duevski7, Ron M. Heeren8, Shane Ellis9, David P. Fenning10 and Erik Garnett11; 1AMOLF, Amsterdam, Netherlands; 2University of California, San Diego, San Diego, California, United States; 3Maastricht University, Maastricht, Netherlands.

Grain boundaries play a key role in the performance of thin-film optoelectronic devices, yet their effects in halide perovskite materials are still not understood. The biggest factor limiting progress is the inability to identify grain boundaries. Non-crystallographic techniques can misidentify grain boundaries, leading to conflicting literature reports about their influence; however, the gold standard – electron backscatter diffraction (EBSD) – destroys halide perovskite thin films. We solve this problem by using a solid-state EBSD detector with 6,000 times higher sensitivity than the traditional phosphor screen and camera. Correlating true grain size with photoluminescence lifetime, carrier diffusion length and mobility, shows that grain boundaries are not benign but have a recombination velocity of 1670 cm/s, comparable to that of crystalline silicon. We also observe amorphous grain boundaries that give rise to locally brighter photoluminescence intensity and longer lifetimes. This anomalous grain boundary character offers a possible explanation for the mysteriously long lifetime and record efficiency achieved in small-grained halide perovskite thin films. It also suggests a new approach for passivating grain boundaries to lead to even better performance in optoelectronic devices.

ET05.06.03


Hybrid organic-inorganic halide perovskites have emerged as a new family of optoelectronic materials because of their wide tunability in structural and optoelectronic properties. In this work, we focused on the investigation of A-site cations on the structural and optoelectronic properties of perovskites with a formula Ax(MA0.17FA0.83)1-xPb1-ySny(I0.83Br0.17)3, where A are Cs+, Rb+, and guanidinium (GA+), or Cs+-GA+ and Rb+-GA+ with x = 0 – 0.2, and y = 0 – 1.0. Because of the smaller ionic radii of Cs+ (1.8 Å) and Rb+ (1.52 Å) than methylammonium (MA+, 2.16 Å), formamidinium (FA+, 2.53 Å) and GA+ (2.78 Å), adding Cs+ and Rb+ pushes the Goldschmidt tolerance factor into the cubic perovskite phase regime for each Sn composition while adding GA+ leads to an opposite direction. We prepared densely-packed, pinhole-free perovskite films with one-step solution process with mixed solvents plus anti-solvent wash method followed by thermal annealing. X-ray diffraction (XRD) patterns show pure cubic phase for all composition perovskites. The lattice parameter of these perovskites show non-linear lattice parameter versus Sn composition for each A composition with alloyed Pb-Sn having larger lattice parameters than those of pure Pb or Sn perovskites. However, a linear decrease or increase of lattice parameter versus A composition with each fixed Sn composition. The bandgaps deduced from the UV-Vis absorption spectra edges show that the bandgaps decrease with the increasing of Sn to the minima around 75% Sn and then increased to pure Sn. In Pb-rich perovskites, adding Cs+ or Rb+ decreases the bandgaps for each fixed Sn composition, while in Sn-rich perovskites, it causes the decrease of bandgaps. The mechanism of A-site cations on the structural and optoelectronic properties of Pb-Sn and pure Sn perovskites will be discussed based on their impacts on B-X orbital overlap, BX6 octahedral tilting, and strain tolerance. In addition, we also fabricated solar cells with the p-i-n structure and achieved a record maximum PCE of 9.61% for a low band gap (1.26 eV) perovskite of Cs0.16(MA0.07FA0.93)0.07Pb0.78Sn0.22I0.83Br0.17. Moreover, this 75% Sn device can retain 80% of initial PCE after 30 days storage in inert condition followed by over 100 hours in ambient condition.

Overall, this study demonstrated the impact of A-site cations on structural and optoelectronic properties of Pb-Sn and pure Sn double halide perovskites and provides a route to enhance phase and device stability for high Sn or pure Sn perovskite solar cells.

ET05.06.04

Minimizing Non-Radiative Losses Through Rational Defect Passivation for High Performance Perovskite Light-Emitting Diodes Weidong Xu1 and Feng Gao1; 1Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping, Sweden; 2Institution of Advanced Materials (IAM), Nanjing Tech University, Nanjing, China.

Minimizing defect-mediated non-radiative recombination is crucial for the fabrication of high-performance perovskite optoelectronic applications, e.g. perovskite light-emitting diodes (PeLEDs). We demonstrate a rational defect engineering strategy for substantial mitigation of non-radiative losses, including both molecular designing on passivating agents (PAs), and a modified passivation techniques. With using the optimal PA, the well defect-engineered perovskite films enable the preparation of high performance PeLEDs with a high maximum external quantum efficiency (EQE = 18.9%) and a large radiance of 316 W sr⁻¹ m⁻². Importantly, our research reveals the key factor in determining the passivation effect, and provides a useful guideline for promoting passivation effects.

ET05.06.05

Electrode Polarization and Role of Polaron at Methylammonium Lead Halide Perovskite Interfaces Mahshid Ahmadi1, Maximilian Heres1, Emmanuel Mapes2, Eric Lukos3, Juan Bisquert4, Joshua Sangoro5 and Bin Hu1; 1Joint Institute for Advanced Materials, University of Tennessee, Knoxville, Tennessee, United States; 2Institute of Advanced Materials, Universitat Jaume I, Castello, Spain; 3Chemical and Biomolecular Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 4Nuclear Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.
Electrode polarization is a universal phenomenon taking place at the interface between a metallic electrode and an ionic/electronic semiconductor which needs to be studied in detail for organometallic halide perovskite (OMHP) devices. In general, interfaces between hybrid perovskite and electrode or charge transport layers are gaining more attention as studies showed that interfaces can significantly control the operation of hybrid perovskite devices as well as long term performance stability. Previously, the increase of dielectric permittivity in low frequencies <100 kHz in thin films of OMHP was attributed to the ionic migration and accumulation at the interface and space charge polarization enhanced along grain boundaries. It was suggested that long range ion diffusion under external field would be the governing mechanism at low frequencies. In order to gain insight on the origin of dielectric permittivity at low frequency regime here, we study single crystals of MAPbI₃, excluding polarization enhanced through grain boundaries effect. This study is done using broadband dielectric spectroscopy (BDS) in dark condition by varying temperatures and external biases. Generally, there are three sources contributing to the conduction in OMHPs including ions, electrons and holes and polarons. So far, the atomistic origin of slow dynamic process in OMHPs was explained by the transport of ionic species and the drift and/or diffusion of polarons was totally overlooked. In our ac conductivity measurements, we observed that the conductivity decreases with decreasing frequency and temperatures. The accumulation of ions at the interface usually block the carriers from conduction and conductivity is expected to drop at this region. In this study we found that at low frequencies, there is a plateau in ac conductivity. This conductivity is only dropped if a large bias is applied. The polaronic nature of charge carriers in OMHPs has been demonstrated but the transport, migration and accumulation of polarons at the interfaces was not explored. It was suggested that small polarons which transfer through hopping mechanism may not directly contribute in the overall carrier mobility unlike large polarons but they can form charge accumulations states. Here, we conclude that ion migration and accumulation is not solely responsible for giant dielectric constant at low frequency in OMHPs but also there is an effective role from polarons. Indeed, polarons can migrate and accumulate at the interface first. This study opens a way for better understanding of a key aspect in the operation of highly efficient OMHP devices.

References:

ET05.06.07
Tuning the Electronic and Defect Properties of Methylammonium Lead Bromide via Composition Engineering Arun Kumar Mannodi Kanakkithodi, Ji-Sang Park, Duyen H. Cao, Nari Jeon, Alex Martinson and Maria K. Chan; Argonne National Laboratory, Lemont, Illinois, United States.

Methylammonium lead bromide (MAPbBr₃) has grown in prominence as an attractive photovoltaic (PV) absorber owing to its higher stability compared to MAPbI₃, and its desirable electronic, absorption and defect properties which can be further tailored by composition engineering. Inspired by recent work on partial substitution of Pb in MAPbBr₃ by Cobalt to yield additional energy states within the semiconductor band gap leading to intermediate band photovoltaics (IBPVs), we explore the possibility of substituting Pb by various other elements selected from across the periodic table in a high-throughput fashion. Using state-of-the-art density functional theory (DFT) computations, we study the crystalline and electronic structure as well as the energetics of 1/8th substitution of Pb in a MAPbBr₃ supercell by all cationic elements from periods 2, 3, 4, 5 and 6. Both the density of states and the calculated charge transition levels are used to probe the energy states created by the substituent atom in the electronic structure of MAPbBr₃, revealing several substituents that create mid-gap energy states while retaining the parent band gap (~ 2 eV at the PBE level of theory). Formation energies of substituent defects are calculated in various charged states and compared with the energetics of dominant intrinsic defects, established as the vacancy defects Nb, Sc, and group V element Sb create low formation energy defects that compensate for the dominant intrinsic defects and shift the equilibrium Fermi level closer to the conduction band minimum, making the semiconductor conductivity more n-type. The relative stability of these substitution defects coupled with the fact that they produce mid-gap energy levels not only makes them promising candidates for IBPV's but raises the possibility of these impurities creating deep trap states in the MAPbBr₃ band gap that can cause harmful non-radiative charge carrier recombination and reduce the PV efficiencies. Further, many of the promising substituents thus identified were experimentally synthesized and characterized, and the measured absorption coefficients compared favorably with the computed spectra. Lastly, machine learning techniques were applied on the high-throughput computational data to yield simple predictive models for the substituent transition levels as a function of structural and electronic features derived from a significantly cheaper unit cell calculation on a completely Pb-substituted hybrid perovskite.

REFERENCES

ET05.06.08
Light-Induced Dynamic Chemical and Structural Disorder in Mixed Halide Hybrid Perovskites Tim W. van de Goor, Sian E. Dutton and Felix Deschler; University of Cambridge, Cambridge, United Kingdom.

Mixed halide hybrid perovskites are highly efficient semiconductors with promising applications in optoelectronics. Defects and disorder dictate the properties of this material. Structural disorder can be defined as local variations in the crystal structure, whereas chemical disorder refers to local inhomogeneities in material composition. Both types of disorder are highly dynamic and are likely responsible for the favourable (e.g. long carrier lifetimes) and unfavourable (e.g. the Hoke effect) properties observed in this material. In the rapidly maturing field of hybrid perovskite optoelectronics, where the hunt is now on for the best performing material composition, little attention is given to the fundamental role of disorder. Here we aim to elucidate the relevant time- and length- scales for both types of dynamic disorder in this material, with the aim of gaining a better understanding of their relation to the optoelectronic properties. In particular, we use a combination of structural and thermodynamic techniques to investigate transitions in the prototypical mixed halide hybrid perovskite CH₃NH₃PbBr₃I₁₋ₓBrₓ. We use temperature dependent powder X-ray diffraction and heat capacity measurements under illumination to quantify the nature of — and energy associated with light-induced order/disorder transitions.

References

ET05.06.09
Controlled Nucleation and Growth for Optimum Perovskite Film Morphology at Liquid-Electrolyte Interface—A Study by Electrochemical
Perovskite Solar Cells (PSCs) have already attracted considerable attention attributed to its intriguing properties, showing a tremendous jump in efficiency from 3.8%\(^1\) by Kojima et al. (2009) to 22.1%\(^2\) by Yang et al. (2017). A lot of research has been done on the efficiency improvement of PSCs by optimization of the film morphology at the interfaces in the device. Analyzing these interfaces by various characterization techniques including electrochemical impedance spectroscopy (EIS) in a solid state active device geometry is not only difficult to decipher but sometimes is misleading as well since there may be multiple processes occurring at similar time scale at multiple interfaces.

To simplify the analysis of the perovskite films EIS should be carried out in perovskite-liquid electrolyte interface. Recently, Li et al. have measured the flat band potential, charge carrier density and type of charge carrier accumulation at the perovskite-liquid interface from Mott-Schottky plot for spin coated and spray coated films of methylammonium lead tri-iodide (MAPbI\(_3\)) perovskite.\(^3\)

In this work, MAPbI\(_3\) perovskite has been synthesized by one step spin coating of lead acetate-trihydrate and methylammonium iodide precursor on pre-heated substrate. Significant difference in film morphology has been observed as the substrate temperature \(T_{sub}\) varied from room temperature to 120 °C prior to spin coating. Nucleation and growth mechanism is revisited to find out the coating. Nucleation and growth mechanism is revisited to find out the coating. We have measured the Urbach energy and a slow decrease of their optical band gap energy.

Previously, we have measured the Urbach energy and a slow decrease of their optical band gap energy.\(^4\) Recent investigations have revealed that the Urbach energy is correlated well with the loss in the open-circuit voltage \(V_{OC}\) of optimized cells, compared to their bandgap \(^1\). When cooling CH\(_3\)NH\(_3\)PbI\(_3\) film we find a substantial decrease in the Urbach energy and a slow decrease of their optical band gap energy.

The photovoltaic performance of world-leading Organic-inorganic halide perovskite (OHP) solar cells remains limited by defective electronic states, which introduce non-radiative recombination pathways for charge carriers. In OHP thin films, it is emerging that surface defects are the most prevalent and thus have the largest impact on luminescence and device efficiency. We have recently shown that the addition of potassium halides can increase luminescence yield substantially but the direct impact on carrier traps has not yet been elucidated.

Here, we employ a state-of-the-art photoemission electron microscopy (PEEM) setup to map local surface defect states on triple cation, mixed-halide perovskite films by inert electrospinning technique is presented. Morphological, as well as optical/photonic properties have been studied and demonstrated first comprehensive data on electrospun organic-inorganic hybrid materials.

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Here, we employ a state-of-the-art photoemission electron microscopy (PEEM) setup to map local surface defect states on triple cation, mixed-halide perovskite films.\(^5\) In OHP thin films, it is emerging that surface defects are the most prevalent and thus have the largest impact on luminescence and device efficiency. We have recently shown that the addition of potassium halides can increase luminescence yield substantially but the direct impact on carrier traps has not yet been elucidated.

We have probed the temperature dependence of methylammonium lead iodide (CH\(_3\)NH\(_3\)PbI\(_3\)) absorption spectra. We extract the Urbach energy as the reciprocal of the slope of the absorption band edge in logarithmic scale. Its value depends on the material disorder and generally correlates well with the loss in the open-circuit voltage \(V_{OC}\) of optimized cells, compared to their bandgap \(^1\). When cooling CH\(_3\)NH\(_3\)PbI\(_3\) film we find a strong decrease in their Urbach energy and a slow decrease of their optical band gap energy.

Electrospun Perovskite Fibers – New Flexible 1D Nanocomposites for Light Harvesting Applications

The photovoltaic performance of world-leading Organic-inorganic halide perovskite (OHP) solar cells remains limited by defective electronic states, which introduce non-radiative recombination pathways for charge carriers. In OHP thin films, it is emerging that surface defects are the most prevalent and thus have the largest impact on luminescence and device efficiency. We have recently shown that the addition of potassium halides can increase luminescence yield substantially but the direct impact on carrier traps has not yet been elucidated.

Here, we employ a state-of-the-art photoemission electron microscopy (PEEM) setup to map local surface defect states on triple cation, mixed-halide perovskite films.\(^5\) In OHP thin films, it is emerging that surface defects are the most prevalent and thus have the largest impact on luminescence and device efficiency. We have recently shown that the addition of potassium halides can increase luminescence yield substantially but the direct impact on carrier traps has not yet been elucidated.

Finally, we examine how increasing levels of potassium doping affect the local carrier trapping dynamics by integrating PEEM with time-resolved pump-probe spectroscopy. This enables us to monitor the rate and intensity of photoexcited hole trapping into these intra-band surface states. When teamed with the spatial resolution of PEEM beyond the diffraction limit, such time-resolved measurements provide a uniquely powerful tool for characterising defect states, both in local regions and across larger regions of films.

Relation Between Absorption and Electronic Properties of Organic-Inorganic Halide Perovskites

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From the theoretical Urbach energy temperature dependence we obtain an average energy of electronically active phonon states of 110 ± 20 cm\(^{-1}\), which implies that the dynamic disorder of CH\(_3\)NH\(_3\)PbI\(_3\) is mainly caused by cage vibrations \(^2\). This gives further evidence that the density of active static defects in perovskites is very low in comparison to other materials used for solar cells, including bulk monocrystal semiconductors.

By comparing the photoconductivity and emission-based absorption spectroscopies, we find that the CH\(_3\)NH\(_3\)PbI\(_3\) band structure is slightly indirect. This
may be caused by spin-orbital coupling, the so-called Rashba splitting effect. Our results prove the direct nature (non-phonon assisted) of both absorption and emission in CH₃NH₃PbI₃. The experimentally observed long photoluminescence decay time is given by small overlap between free electrons and holes in the k space.

Finally, we found a strong correlation between the VOC deficiency, compared to the bandgap, of finalized solar cells and Urbach energies measured by PL spectroscopy. These results will help to establish more refined practical efficiency limits of perovskite solar cells by taking into account the Urbach energy, to be compared to the Shockley-Queisser limit, which only considers the bandgap.


ET05.06.13
Feasibility of Quantum Dot Based Lasers in Blue and Green Region

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Inorganic lead halide perovskite (CsPbX₃: X: Cl, Br, I) nanocrystals (NCs) are well-known for their high photoluminescence (PL) efficiency and stability as compared to organic lead halide perovskite. The high PL yield of these NCs makes them an ideal candidate for light emitting applications with broader tunability (400 to 700 nm). Replacing anions in CsPbX₃ from Cl to Br to I yields PL emission in blue, green and red region. In the present work, we demonstrate facile lasing tunability at low threshold in CsPbBr₃ and CsPbCl₃ quantum dots. These quantum dots (QDs) were synthesized by the reported hot injection wet chemical method. The size of CsPbBr₃ QDs is 5.5 ± 0.98 nm as calculated from the transmission electron microscopy image analysis. The measured PL yield of these QDs is about 95% having full width at half maximum 132 meV without any passivating layer of other semiconductor material (like core shell CdSe/CdS QDs). Temperature dependent PL study in the range 10 K-300 K gives the small value of exciton-longitudinal phonon coupling (49.4 meV) with high exciton binding energy (50 meV). The PL spectrum recorded at 10 K under xenon lamp excitation shows the excitonic luminescence feature at 2.42 eV and a hump type feature at 2.38 eV. If the same sample is excited using a pico-second laser, it is observed that the low energy feature evolves into a sharp peak having very high intensity as compared to the excitonic peak intensity. The low energy peak is attributed to the stimulated emission peak as a result of bieexcitonic recombination. The sign of stimulated emission is observed under low excitation of xenon lamp (~4.16 mW) and is the effect of high bieexcitonic binding energy (40 meV) which avoids the re-absorption of bieexcitonic photon in excitonic peak.

As we change the composition of halide i.e. Br to Cl the emission changes from green to blue. The size of CsPbCl₃ QDs is about 5.3 ± 1.1 nm and shows emission at 3.04 eV with full width at half maximum of 97 meV. The PL yield of these QDs is very low ~7% at room temperature but at low temperature (10 K) PL intensity shows 90 times enhancement as compared to room temperature. At low temperature excitonic peak is observed at 3.022 eV and bieexcitonic peak is at 2.97 eV. The bieexcitonic binding energy of about 50 meV is observed in these QDs.

By changing the halide composition in CsPb(Br,Cl); QDs one can tune the emission and lasing action from blue to green region of visible region. The notable result is in CsPbBr₃, and CsPbCl₃ QDs reveal the stimulated emission. At low temperature, bieexcitonic feature appears well resolved (which yield stimulated emission) while at room temperature, fitting of the data is required to distinctly observe the bieexcitonic feature. The high PL emission yield, large excitonic ad bieexcitonic binding energy and defect tolerant nature of these QDs makes them an ideal candidate for low threshold based quantum dot lasers.

ET05.06.14
Efficient NTSC Blue and White Perovskite Light Emitting Diodes via Mu Doping at B-Site

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Lead halide perovskite have been dominating the optoelectronic field for last several years. Particularly, due to the superior optical properties, colloidal nanocrystals of CsPbX₃ are finding great opportunities in quantum dot light emitting diodes (QLEDs). Green and red nanocrystals are progressing rapidly in QLEDs with efficiencies 12.9% and 6.8% respectively.¹ Blue nanocrystals, however, are still lagging far behind red and green owing to their poor PLQYs. The best efficiency reported on these blue perovskite QLEDs is only 0.07%.² Our group, recently discovered that in addition to the PLQYs, the transport layers are limiting the performance of the LEDs. By employing a combination of HTL and a buffer layer (TFB:PFI), we achieved ~7-fold increase in the efficiency to 0.5%.³ Further, we improved the quality of nanocrystals by doping with Mn, which eventually lead to a factor of 4x enhancement in the PLQYs. The best efficiency reported on these blue perovskite QLEDs is only 0.07%.³ Our group, recently discovered that in addition to the PLQYs, the transports layers are limiting the performance of the LEDs. By employing a combination of HTL and a buffer layer (TFB:PFI), we achieved ~7-fold increase in the efficiency to 0.5%.³ Further, we improved the quality of nanocrystals by doping with Mn, which eventually lead to a factor of 4x enhancement in the PLQYs. The best efficiency reported on these blue perovskite QLEDs is only 0.07%.³ Our group, recently discovered that in addition to the PLQYs, the transports layers are limiting the performance of the LEDs. By employing a combination of HTL and a buffer layer (TFB:PFI), we achieved ~7-fold increase in the efficiency to 0.5%.³ Further, we improved the quality of nanocrystals by doping with Mn, which eventually lead to a factor of 4x enhancement in the PLQYs. The best efficiency reported on these blue perovskite QLEDs is only 0.07%.³ Our group, recently discovered that in addition to the PLQYs, the transports layers are limiting the performance of the LEDs. By employing a combination of HTL and a buffer layer (TFB:PFI), we achieved ~7-fold increase in the efficiency to 0.5%.³ Further, we improved the quality of nanocrystals by doping with Mn, which eventually lead to a factor of 4x enhancement in the PLQYs. The best efficiency reported on these blue perovskite QLEDs is only 0.07%.³ Our group, recently discovered that in addition to the PLQYs, the transports layers are limiting the performance of the LEDs. By employing a combination of HTL and a buffer layer (TFB:PFI), we achieved ~7-fold increase in the efficiency to 0.5%.³ Further, we improved the quality of nanocrystals by doping with Mn, which eventually lead to a factor of 4x enhancement in the PLQYs.

References

ET05.06.15
Acid-Catalyzed Reactions Activate Solvents in Perovskite Precursor Inks

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Hybrid organic-inorganic perovskites (HPs) have been prepared using organoammonium iodide and lead iodide precursor solutions are remarkable absorbing layers for photovoltaic (PV) devices. HPs with mixed cations, specifically those comprising combinations of formamidinium, methylammonium (CH₃NH₃⁺) and cesium cations, have resulted in devices with record-setting efficiencies. Troublingly, recent reports have shown that CH₃NH₃⁺ is consumed through X-ray diffraction on model HOIP films formed with precursor solutions in which CH₃NH₃I is intentionally and stoichiometrically replaced with N,N-Dimethylformamide (DMF) and dimethylsulfoxide (DMSO). A series of experiments involving sequential addition of precursors to DMF/DMSO solvent mixtures before and after thermal annealing of the precursor solutions suggest that reaction of CH₃NH₃⁺ with DMSO produces dimethylammonium, (CH₃)₂NH⁺ during solution annealing. X-ray diffraction on model HOIP films formed with precursor solutions in which CH₃NH₃⁺ is intentionally and stoichiometrically replaced with N,N-Dimethylformamide (DMF) and dimethylsulfoxide (DMSO). A series of experiments involving sequential addition of precursors to DMF/DMSO solvent mixtures before and after thermal annealing of the precursor solutions suggest that reaction of CH₃NH₃⁺ with DMSO produces dimethylammonium, (CH₃)₂NH⁺ during solution annealing.

Our studies elucidate the chemistries that take place between CH₃NH₃⁺ and commonly-used processing solvents, N,N-Dimethylformamide (DMF) and dimethylsulfoxide (DMSO). A series of experiments involving sequential addition of precursors to DMF/DMSO solvent mixtures before and after thermal annealing of the precursor solutions suggest that reaction of CH₃NH₃⁺ with DMSO produces dimethylammonium, (CH₃)₂NH⁺ during solution annealing.
Halide perovskites are inexpensive and easily processable next generation semiconductors. We here demonstrate perovskite solid-state confinement in nanoporous oxide matrices as a general strategy to control the size of the nanocrystallites (<10 nm) in the strong quantum size effect region. Photoluminescence tuning between near infrared and ultraviolet is achieved by manipulating the size of perovskite crystals through confinement in nanoporous alumina (npAAO) or silicon (npSi) scaffolds [1]. Our novel method of nanocrystalline perovskites preparation within a porous oxide matrix results in device-relevant structure that requires no colloidal stabilization. Low-voltage LEDs with narrow, blue-shifted emission fabricated with perovskite nanocrystallites confined within npAAO thin films support the general concept for next-generation photonic devices. The template-controlled size of the perovskite crystals is quantified in npSi with microfocus high-energy X-ray depth profiling in transmission geometry, verifying the growth of perovskite nanocrystals throughout the entire thickness of the nanoporous films. We study in detail exciton recombination, exciton-phonon interactions and energy trap states in confined and bulk semiconductor films using low temperature photoluminescence spectroscopy down to 3.8 Kelvin.

Further areas of application include photon detectors, (polarized) electroluminescent devices, single-photon sources and metasurfaces. Future developments will include increasing the efficiency of the LEDs, exploring their applications in flexible devices and in depth study of the fundamental properties of the confined structures.


ET05.06.16
Metal-Halide Perovskite Quantum Dots in Nanoporous Thin Films for Optoelectronic Applications
Stefan Demchynshyn, Serdar Sariciftci, Markus Scharber, Siegfried Bauer and Martin Kaltenbrunner; Johannes Kepler University, Linz, Austria.

Halide perovskites are inexpensive and easily processable next generation semiconductors. We here demonstrate perovskite solid-state confinement in nanoporous oxide matrices as a general strategy to control the size of the nanocrystallites (<10 nm) in the strong quantum size effect region. Photoluminescence tuning between near infrared and ultraviolet is achieved by manipulating the size of perovskite crystals through confinement in nanoporous alumina (npAAO) or silicon (npSi) scaffolds [1]. Our novel method of nanocrystalline perovskites preparation within a porous oxide matrix results in device-relevant structure that requires no colloidal stabilization. Low-voltage LEDs with narrow, blue-shifted emission fabricated with perovskite nanocrystallites confined within npAAO thin films support the general concept for next-generation photonic devices. The template-controlled size of the perovskite crystals is quantified in npSi with microfocus high-energy X-ray depth profiling in transmission geometry, verifying the growth of perovskite nanocrystals throughout the entire thickness of the nanoporous films. We study in detail exciton recombination, exciton-phonon interactions and energy trap states in confined and bulk semiconductor films using low temperature photoluminescence spectroscopy down to 3.8 Kelvin.

Further areas of application include photon detectors, (polarized) electroluminescent devices, single-photon sources and metasurfaces. Future developments will include increasing the efficiency of the LEDs, exploring their applications in flexible devices and in depth study of the fundamental properties of the confined structures.


ET05.06.17
Mass Transfer-Tuned Growth Pathways of Colloidal Perovskite Quantum Dots Revealed by a High-Throughput Microfluidic Strategy
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Since the advent of organic/inorganic metal halide perovskites and their expanding application in low cost solution-phase processing of high efficiency optoelectronics, a wide expanse of colloidal synthesis techniques have been developed. However, due to the inherent limitations of batch screening approaches, these studies struggle to effectively characterize large parameter spaces and thereby develop a complete understanding of the fundamental nucleation and growth pathways of perovskite quantum dots (QDs). Recent works in colloidal QD growth characterization have implemented rapid microfluidic screening strategies. However, similar to their flask-based predecessors, these flow studies have not accounted for the effect of reactant mixing rates which are known to significantly influence growth pathways in the controlled synthesis of perovskite nanocrystals.

Herein, we present a systematic study of the mass transfer-tuned synthesis for three different cesium-lead-tribromide perovskite nanocrystal reaction strategies using an intelligent microfluidic screening technology. The microfluidic characterization platform consists of modular heated units equipped with a unique in-situ spectral monitoring probe (UV-Vis absorption and fluorescence spectroscopy) which may translate along the 27 cm tubular microreactor reaching 68 sampling ports. Complete platform automation enables high-efficiency collection of inline photoluminescence and absorption spectra spanning four orders of magnitude in residence time (i.e. growth time), from 100ms to 17 min. The portability of the sampling probe allows us to decouple fluid velocity-controlled mass transfer from reaction time.

This microfluidic approach enables rapid discovery, screening, and optimization of colloidal QDs with desired optoelectronic properties via high-throughput screening (>10,000 experimental conditions) of the accessible synthesis parameter space. Utilizing this developed intelligent microfluidic platform, we systematically studied the effect of early mixing timescales on the QD nanocrystal size and size distribution. Varying the average fluid velocity and slug size tunes the degree of mixing within droplets containing the cesium-lead-tribromide precursors, resulting in perovskite nanocrystals with different optoelectronic properties.

ET05.06.18
Lead-Free Perovskite for Highly Sensitive Photodetectors
Chun K. Liu; Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Recently, organic-inorganic lead halide perovskites have emerged as potential light absorbing materials for high-performance photodetectors. However, the toxicity of Pb-containing perovskites significantly hinders their practical applications. Thus, it is necessary to develop lead-free alternatives while maintaining high sensitivity. Herein, we report a lead-free, low-voltage and high-performance photodetector based on a tin perovskite. The device shows broadband photosponse from ultraviolet to near infrared with highest responsivity (R) of 1.7 × 10^5 AW^-1. After vertically heterostructuring the perovskite with an organic semiconductor, the maximum R increases to 2.1 × 10^6 A W^-1, and specific detectivity of 1.5 × 10^12 Jones as well as EQE of 3.8 × 10^6 can be obtained. The impressive performance of the photodetector is due to the superior optoelectronic properties of the tin perovskite and photogating effect originated from the vertical heterojunction. Moreover, the device is also assembled on a flexible substrate, demonstrating both high sensitivity and outstanding bending stability. This work paves the way for realizing non-toxic, low cost and high-performance photodetectors.

ET05.06.19
Digitally Programmable Polarization Anisotropy of Perovskite Nanowire-Block Copolymer Composites
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Semiconducting nanowires possess unique anisotropic optoelectronic properties arising from quantum-span style="font-size:10.8333px">”</span>and dielectric<span style="font-size:10.8333px">”</span> confinement effects, making them attractive candidates for a wide range of electronic and photonic applications. However, similar to their flask-based predecessors, these flow studies have not accounted for the effect of reactant mixing rates which are known to significantly influence growth pathways in the controlled synthesis of perovskite nanocrystals.
As research on perovskites has rapidly developed in recent years, various research groups have made great efforts to improve the processing and characteristics of perovskite light-emitting devices (PeLEDs). Perovskite has advantages of low material cost and simple process. However, it also has technical issues like short life-time and low stability. In this study, we demonstrated large area PeLEDs that are all-solution processed under ambient condition using organic-inorganic hybrid perovskite compounds as next generation light sources. In this work, an electron transport layer (ETL) was optimized to improve the electrical characteristics, to reduce the operating bias voltage and, to improve the optical characteristics. To improve the electron injection at the interface between the cathode and the perovskite layer, a thin layer of polyethyleneimine (PEI) was spin-coated on the perovskite layer prior to the deposition of the cathode. The PEI could reduce the work function of the cathode; hence, the electron injection barrier was significantly reduced. The electron transport properties of PEI were further improved by simply doping some elements. Solution processable n-type semiconducting materials (Cs2CO3, Alq3, and CsF) were selected as n-type dopant. Also, thin layer of polymethylenemethacrylate (PMMA) was spin-coated on the perovskite layer to reduce the pin-holes in the perovskite layers. As fabricated PeLEDs based on these solution processable materials showed extremely low turn on voltage and high maximum luminance. Also, a silicone encapsulation was used to prevent the device from degradation by moisture and oxygen. The silicone encapsulation materials for commercial LEDS were used. Liquid silicone was coated on the as-fabricated PeLEDs to passivate the devices. Based on our results, the coated liquid silicone did not affect the performance of the PeLEDs. The lifetime of the PeLEDs encapsulated with commercial silicone was good performance which was comparable to the glass-lid encapsulation. Since the silicone was flexible, these encapsulation materials could be used in flexible PeLEDs. The luminescence characteristics of green region were confirmed by using a perovskite compound of MAPbBr3 which is attracting attention as a next generation light source, and its value as a next generation light-emitting devices was confirmed by applying it to a large area flexible device.

Impact of Excess PbI2 on the Structure and the Temperature Dependent Optical Properties of Methylammonium Lead Iodide Perovskites

We investigate the impact of excess PbI2 in the precursor solution on the structural and optical properties of thin films of the model hybrid perovskite methylammonium lead iodide (MAPbI3). We find that excess of PbI2 in the precursor solution results in crystalline PbI2 in the final thin film that is located at the grain boundaries. From UPS we find that this crystalline PbI2 phase has no direct impact on the electronic structure of MAPbI3. In contrast to that, temperature dependent absorption measurements indicate a systematic change in the temperature dependence of the exciton binding energy in the perovskite. We also observe a decrease in the critical temperature and a concomitant smearing out of the tetragonal – orthorhombic phase transition as a function of excess PbI2. Our results thus help to better understand the exact role of PbI2 in the perovskite layer and pave the way for a more tailored design of perovskite solar cell.

Broadband Luminescence in Small Molecule Engineered Hybrid Perovskites

The emerging class of hybrid perovskite systems has attracted immense attention recently due to their uniquely interesting properties which has led to solar cell architectures with very high conversion efficiency. These materials have also been explored for other optoelectronic device applications such as lasing, sensors, photo sensors, light emitting devices (LED). Lately, this class of systems is being further explored for futuristic optoelectronic devices by employing small molecular engineering. Such molecular manipulations have been shown to control the dimensionality and associated photo-physics of these systems such as the electron-hole interactions and excitonic effects. In particular, one sub-group of such hybrid perovskites has exhibited broadband emitting properties which are of great interest as potential materials for white light emitting diodes (LEDs).

The discussion of broadband luminescence in the literature has focused on the identification of the specific contributions to such emission (e.g. bound excitons, self-trapped excitons, STE) and their possible connection to the specific structural features and organic/inorganic components in the system. In this work we report the observation of broadband emission in 1D ribbon system of (H$_2$N-CH$_2$-CH$_2$-NH$_2$)$_8$(Pb$_4$Br$_{18}$)●Br$_6$ as well as 2D corrugated system of (H$_2$N-CH$_2$-CH$_2$-NH$_2$)$_2$(Pb$_2$Cl$_6$)●Cl$_2$. The common amine used was ethylene diamine (En), which is the smallest amine not used thus far in this context. We have employed several techniques such as single crystal x-ray diffraction (SC-XRD), steady state photoluminescence (PL), UV-absorbance, diffused reflectance spectroscopy (DRS), time resolved photoluminescence (TRPL) and Raman spectroscopy to study and compare the structural and optical properties of the two materials as well as their respective diammonium salts. Our studies have brought out structure-specific contributions and interplay of the molecular and STE contributions. The primary absorption process appears to be driven by the molecular component while the STE appears to be centered on the inorganic component which may involve the intrinsically heightened polarization at the organic-inorganic interface. Distortions can be important for localization but do not appear uniquely control this phenomenon.

Electronic Structure Analysis of an Organometallic Halide Perovskite via Photoemission Yield Spectroscopy in Air at Various Temperature

An open counter [1] is a unique detector that can operate in air at atmospheric pressure to detect and count a small number of low-energy photoelectrons. Therefore, photoemission yield spectroscopy in air (PYSA) can be performed by employing an open counter as the detector. Recently, PYSA measurement was performed at various temperatures [2-4] and its applicability to the analysis of temperature dependence on the change of work function was.
demonstrated [3, 4]. In these cases, PYSA measurement was performed as follows. UV light emitted from a deuterium lamp was monochromatized using a
grating monochromator, which was then focused onto the sample surface. The number of photoelectrons emitted from the sample surface was counted using
an open counter. During the measurement, the sample temperature was controlled using a small heater connected to a temperature controller. This method
was considered effective for the comparison of the electronic structures of materials that exhibit different properties at high temperatures. Temperature
effects of CH₃NH₃PbI₃ perovskite solar cells having simple planar architecture were reported [5]. According to this report, the obvious changes in the
crystal structure which seriously affects the performance of the solar cells were found. Therefore, PYSA was applied to analyze the change in the electronic
structure of CH₃NH₃PbI₃ at various temperatures. We discussed the change in the threshold energy of photoemission, which corresponds to the first-
ionization potentials, at around the phase transition temperature of the perovskite.


ET05.06.24
Charge Transport in Surface-Guided CsPbBr₃ Nanowires Ella Sanders, Eitan Oksenberg and Ernesto Joselevich; Materials and interfaces, Weizmann Institute of Science, Rehovot, Israel.

Although metal halide perovskites (MHPs) have emerged as exceptional materials for optoelectronics, their charge transport properties remain under
scientific debate. One of the reasons for this is that most charge transport measurements are conducted on polycrystalline thin films, which adds complexity
to the system and makes it difficult to interpret the results in an unambiguous way. In this work, we concentrated on surface-guided planar nanowires of
CsPbBr₃, single crystals with a 1D nature, which serve as a simplified model system for charge transport measurements. The surface-guided growth of
MHP nanowires on sapphire results in ordered and well-defined arrays, which can be easily integrated into functional devices. We studied the charge
transport in these arrays as well as in individual CsPbBr₃ nanowires, all having uniform crystallographic orientation and well-defined facets. We fabricated the first field-effect transistor on a single nanowire of MHPs and measured charge transport characteristics such as field-effect mobility and charge carrier
concentration. We also observed intriguing time-dependent electrical behavior in dark and under illumination, related to the dynamic nature of these soft
semiconductors. Surface-guided growth of MHP nanowires enables fast, simple and efficient fabrication of multiple devices in parallel manner for
fundamental research and optoelectronic applications.

ET05.06.25
Photoluminescence Spectroscopy of Halide Perovskites Stuart Thomson; Edinburgh Instruments, Livingston, United Kingdom.

Halide perovskites are a promising new class of semiconducting materials for a wide variety of optoelectronic applications, such as photovoltaics, light
emitting diodes, lasers and optical sensing. They have received widespread attention due to their many attractive synthetic and photophysical properties,
namely; solution processability, high tunability, long charge carrier lifetimes and high charge carrier mobilities. Photoluminescence spectroscopy is a
powerful tool for the photophysical investigation and materials optimisation of halide perovskites. Using photoluminescence spectroscopy we have
investigated the photophysics of a range of halide perovskite photovoltaic absorbers and light emitters.

Methyl ammonium lead iodide (MAPI) is one of the most efficient and widely investigated perovskite absorbers for photovoltaic cells. Using time-resolved
photoluminescence, the charge carrier lifetime of MAPI was measured and was found to increase with the thermal annealing duration of the perovskite
layer. In addition, temperature dependent photoluminescence spectroscopy was used to monitor the change in the perovskite bandgap with temperature and
determine the orthorhombic to tetragonal and tetragonal to cubic phase transition temperatures.

Photoluminescence spectroscopy is particularly well suited for the study of perovskite materials for light emitting applications. Two dimensional
perovskites are a promising material for the creation of single component white light source. We investigated the two dimensional white light emitter, α-
(DMEN)PbBr₃, using steady state photoluminescence to determine the chromaticity coordinates of the emission and time-resolved photoluminescence to
probe the excited state lifetimes.

ET05.06.26
Elucidating Exciton-Phonon Interaction in Quasi-2D Ruddlesden-Popper Perovskites Watcharaphol Paritmongkol1, Nabeel S. Dahod2, Alexia
Stollmann1,2, Shao-Liang Zheng3 and William Tisdale2; 1Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United
States; 2Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Mechanical and Process Engineering,
ETH Zürich, Zürich, Switzerland; *Corresponding author. Harvard University, Cambridge, Massachusetts, United States.

Two-dimensional lead halide perovskites (2D LHPs) are solution-processed semiconductor quantum wells with great promise for optoelectronic
applications. Their properties are highly tunable, and can be modified by changing the quantum-well thickness as well as their chemical constituents. Since
2D LHPs have high exciton binding energies, understanding exciton dynamics is important for designing novel 2D LHP devices. Here, we present a study
based on temperature-dependent photoluminescence to elucidate exciton-phonon interactions in these materials. Our study is based on iodide perovskites
with varied quantum-well thicknesses, cations, and organic spacer lengths. The results show that tuning these parameters affects photoluminescence
properties as well as phase transitions. This study provides a fundamental understanding of 2D LHP photophysics, necessary for developing novel 2D LHP
optoelectronics.

ET05.06.27
Time-Resolving Ultrafast Polaron Formation Dynamics in Lead-Halide Perovskites via Terahertz Emission Spectroscopy Burak Guzelturk1, 2 and
Aaron Lindenberg1, 2; 1Stanford University, Stanford, California, United States; 2SLAC National Accelerator Laboratory, Menlo Park, California, United
States.

Recently we have revealed that poly-crystalline thin-films of hybrid lead-halide perovskites emit broadband electromagnetic radiation within the terahertz
(THz) frequency window [1]. This radiation mainly arises from ultrafast electron-hole separation due to different diffusivities of photo-generated carriers
(i.e., photo-Dember effect). A transient photocurrent with a rise-time shorter than the period of an optical phonon mode can coherently drive the
responding phonon. By means of this, longitudinal optical (LO) phonons can be coherently launched via ultrafast photo-excitation and can be detected
via measurement of the associated THz emission [1, 2]. In a polaron picture, a carrier alters the equilibrium position of ions within a polar semiconductor
and this effectively induces a potential well for the carrier causing its “self-trapping” around the displaced ions [3]. Polaron formation proceeds through
long range carrier – LO phonon coupling [4] and was lately evoked to account for the surprising opto-electronic properties of the hybrid perovskites [5].
Here we show that we can time-resolve polaron formation dynamics via monitoring of the emitted THz radiation from the coherent LO phonon mode. In MAPbI₃, we observe a strong emission peak at 1.15 THz corresponding to the lowest energy LO phonon mode of the inorganic sub-lattice. By time- and frequency-resolving this LO phonon-associated emission, we observe an intriguing dependence on the excitation photon energy. When we excite the perovskite at its band-edge (770 nm), the emission at the LO mode arises instantaneously. However, when a well-above bandgap excitation (400 nm) is used, the emission at the LO phonon mode emerges with a finite time delay (~300 fs). This suggests that hot-carriers cannot form polarons due to their excess kinetic energy. Therefore, initial carrier cooling dominates over the polaron formation. Furthermore, we observe a dynamic softening of the LO mode within the first ps suggesting that electronic charge alters the stiffness constant of the ionic bonds within the material as predicted in other polaronic systems [3].


**ET05.06.28**

**Lead Halide Perovskites Nanocube Superlattice and the High-Pressure Chemistry**

**Yasutaka Nagaoka and Ou Chen**; Brown University, Providence, Rhode Island, United States.

Lead halide perovskites are promising materials for a range of applications owing to their structural uniqueness and optoelectronic properties. Understanding the relationship between the atomic/superstructures and the associated properties of perovskite materials is vital to fully utilize their potential performances. We present the detailed pressure processing of CsPbBr₃ perovskite nanocube superlattices (NC-SLs) for the first time. By using diamond anvil cell combined with in situ synchrotron-based small/wide angle X-ray scattering (SAXS and WAXS) and photoluminescence (PL) probes (shown A in the Figure), the NC-SL transformations are correlated at both atomic and superlattice levels with the PL transition through a pressure cycle of 0 ↔ 17.5 GPa. In-situ SAXS and WAXS measurements monitored its mechanical and structural changes showing that the NC-SL went through multiple phase transitions both at atomic and superlattice levels. After the pressure process, the individual CsPbBr₃ NCs fused into two-dimensional nanoplatelets (NPLs) with a uniform thickness (~10.1 nm). The pressure-synthesized perovskite NPLs exhibited a pure single cubic crystal structure, a 1.6-fold enhanced photoluminescence quantum yield, and a longer emission lifetime than the starting NCs. These results suggest that pressure processing can provide a novel approach for the quick conversion of lead halide perovskites into structures with enhanced properties.

**SESSION ET05.07: (In)Stability and Degradation**

**8:00 AM ET05.07.01**

*Instability of Lead Halide Perovskites* **Yabing Qi**; Okinawa Institute of Science and Technology, Okinawa, Japan.

Instability issues associated with lead halide perovskite materials and solar cells have captured a significant amount of research attention. My group at OIST investigates these materials to obtain deepened understanding of degradation mechanisms. In this talk, I will present our findings on degradation of lead halide perovskites and the strategies to overcome some of the instability issues.

**8:15 AM ET05.07.02**

*Defect Physics and (In)Stability in Metal-Halide Perovskite Semiconductors* **Annamaria Petrozza**; Istituto Italiano di Tecnologia, Milano, Italy.

Semiconducting metal-halide perovskites present various types of chemical interactions which give them a characteristic fluctuating structure sensitive to the operating conditions of the device, to which they adjust. This makes the control of structure-properties relationship, especially at interfaces where the device realizes its function, the crucial step in order to control devices operation. In particular, given their simple processability at relatively low temperature, one can expect an intrinsic level of structural/chemical disorder of the semiconductor which results in the formation of defects. Metal halide perovskites have been successfully applied as optically active layers in photovoltaic and optoelectronic devices. The high efficiency of such research-scale devices hold the promise for an imminent application of perovskites in large scale energy production and lighting solutions. Intrinsic thermal and photo-physical instability of these materials pose, however, a challenge for further developments in device scale up and long-term reliability. Instabilities are manifested as light-induced ion migration and segregation, eventually leading to material degradation under prolonged exposure to light. Understanding, controlling and eventually blocking such material instabilities are fundamental steps towards large scale exploitation of perovskite in optoelectronic devices. By combining photoluminescence measurements under controlled conditions with ab initio simulations we identify photo-instabilities related to competing light-induced formation and annihilation of trap states, disclosing their characteristic length and time scales and the factors responsible for both processes. We show that short range/short time defect annihilation can prevail over defect formation, happening on longer scales, when effectively blocking undercoordinated surface sites, which act as a defect reservoir. By an effective surface passivation strategy we are thus able to stabilize the perovskite layer towards such photo-induced instabilities, leading to improved optoelectronic material quality and enhanced photo-stability in a working solar cell. The proposed strategy represents a simple solution towards longer stability perovskite thin films that could be easily implemented in large scale manufacturing.

**8:45 AM ET05.07.03**

*Multicomponent Engineering for Phase Stable, Reproducible and High-Performance Perovskite Materials* **Michael Saliba**; Adolphe Merkle Institute, Fribourg, Switzerland.

Perovskites have emerged as low-cost, high-efficiency photovoltaics with certified efficiencies of 22.1% approaching already established technologies. The perovskites used for solar cells have an ABX₃ structure where the cation A is methylammonium (MA), formamidinium (FA), or cesium (Cs); B is Pb; and X is Br or I. Unfortunately, single-cation perovskites often suffer from phase, temperature or humidity instabilities. This is noteworthy for CsPbX₃ and FAPO₃X which are stable at room temperature as a photoinactive “yellow phase” instead of the more desired photoactive “black phase” that is only stable at higher temperatures. Moreover, apart from phase stability, operating perovskite solar cells (PSCs) at elevated temperatures is required for passing...
industrial norms. Recently, double-cation perovskites (using MA, FA or Cs, FA) were shown to have a stable “black phase” at room temperature. These perovskites also exhibit unexpected, novel properties. For example, Cs/FA mixtures suppress halide segregation enabling band gaps for perovskite/silicon or perovskite/perovskite tandems. (1) In general, adding more components increases entropy that can stabilize unstable materials. Here, we take the mixing approach further to investigate triple cation (with Cs, MA, FA) perovskites resulting in improved reproducibility and stability. (2) We then use multiple cation engineering to integrate the seemingly too small rubidium (Rb) (that never shows a black phase as a single-cation perovskite) to study novel multication perovskites. (3) One composition containing Rb, Cs, MA and FA resulted in a stabilized efficiency of 21.6% and an electroluminescence of 3.8%. The Voc of 1.24 V at a band gap of 1.63 eV leads to a very small loss-in-potential of 0.39 V, one of the lowest measured on any PV material indicating the almost recombination-free nature of the novel compound. Polymer-coated cells maintained 95% of their initial performance at 85°C for 500 hours under full illumination and maximum power point tracking. This is a crucial step towards industrialisation of perovskite solar cells.

Lastly, to explore the theme of multicomponent perovskites further, molecular cations were reevaluated using a globularity factor. Using the multication strategy, we studied an ethylammonium-containing compound that yielded an open-circuit voltage of 1.59 V. (4)

The last part elaborates on a roadmap on how to extend the multication to multicomponent engineering providing a series of new compounds that are highly relevant candidates for the coming years.

(1) McMeekin et al. Science (2016)
(2) Saliba et al., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. EES (2016)
(3) Saliba et al., Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. Science (2016)
(4) Gholipour, ... Saliba, Globularity Selected Large Molecules for a New Generation of Multication Perovskites, Advanced Materials (2017)

9:15 AM ET05.07.04
Anisotropic Moisture Erosion and Carrier Transport in CH3NH3PbI3 Single Crystal Qianrui Lv and Qingsong Yan, Tsinghua University, Beijing, China.

As a new semiconductor material, methyl ammonium lead iodide (CH3NH3PbI3) perovskite has attracted much attention in recent years owing to its outstanding photoelectric properties. Although CH3NH3PbI3 perovskite has achieved tremendous progress in photovoltaic devices, a deeper understanding of its intrinsic physical properties is still of great interest. The anisotropy of properties is an important feature of semiconductor materials, while limited relevant work has been reported regarding the anisotropy in CH3NH3PbI3 perovskite. In this work, we report the fast growth of high-quality CH3NH3PbI3 single crystal by using a non-seeded solution growth method. When exposed the CH3NH3PbI3 single crystal to moisture, it was found that the (001) facet exhibited more sensitive to water molecules and showed faster erosion rate compared with the (100) facet and (112) facet. We then developed a top-down strategy to prepare CH3NH3PbI3 single-crystalline thin films of tens of micrometers in thickness with different orientations, which provided the possibility of directly studying the anisotropy of carrier transport in CH3NH3PbI3 single crystals. Vertical-structured FET devices based on CH3NH3PbI3 single-crystalline thin films with different orientations were fabricated. Compared with the [100] and [112] orientation, it was found that carriers have lower mobility along the [001] orientation than along the [100] and [112] orientation. The origin of the anisotropy in moisture erosion and carrier transport was elucidated from the perspective of crystal structure. The reveal of the orientation-dependent moisture erosion and carrier transport in CH3NH3PbI3 single crystal may deepen the understanding of physical properties of the material and guide the design of stable and high-performance optoelectronic devices in the future.

9:30 AM ET05.07.05
Spiro-MeOTAD Hole Transport Layer in Perovskite-Based Solar Cells Luis K. Ono1, Zafer Hawash1-2, Sonia R. Raga1-3, Emilio J. Juarez-Perez1, Matthew Leyden1-4, Yuichi Kato1-5, Mikas Remeika1-6, Shenghao Wang1-6, Michael V. Lee1-7, Andrew J. Winchester1, Atsushi Gabe1-8, Yan Jiang1 and Yabing Qi1; 1Okinawa Institute of Science and Technology, Okinawa, Japan; 2Department of Engineering and Physics, Karlstads University, Karlstad, Sweden; 3Melbourne Centre of Nanofabrication, Monash University, Melbourne, Victoria, Australia; 4Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka, Japan; 5CNT-Application Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; 6Department of Applied Physics, University of Tsukuba, Tsukuba, Japan; 7Department of Chemistry and Biochemistry, Northern Arizona University, Flagstaff, Arizona, United States; 8Institute of Materials Science, University of Alicante, Sant Vicent del Raspeig, Spain.

In organic-inorganic hybrid perovskite solar cells, optimization of hole transport materials (HTMs) is important for enhancing solar power conversion efficiency and improving stability [1,2]. At OIST, a team of researchers in the Energy Materials and Surface Sciences Unit has been making concerted efforts to study 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-MeOTAD), which is the most widely used HTM in perovskite solar cells [2-8]. In this talk, we will present our latest understanding of fundamental interactions between Li-bis(trifluoromethanesulfonyl)imide (LiTFSI), 4-t-butylpyridine (t-BP) and spiro-MeOTAD. Also, we will show how gas exposure (e.g., exposure to O2, H2O, N2) influences electronic structures and conductivity of such HTM films. In addition, we will propose further strategies to improve perovskite solar cell performance and stability.

Emerging organolead-halide-perovskite-based materials and devices have recently received tremendous attention due to their extraordinary photonic and optoelectronic performance and potential low production costs. Many physical and chemical properties beyond light harvests have erupted. Despite the rapid development of perovskite materials and devices, the impact of environmental factors on different stages of materials synthesis and device fabrication still remains unclear. Moisture or humidity is widely recognized as one of the major lethal factors in perovskite devices degrade or decompose after fabrication. However, recent reports have shown that moisture could be crucial to obtain high-performance perovskite films in a suitable moisture of $\sim 35\%$ relative humidity. Although a few attempts have been made to investigate the morphological evolution of organohalide perovskite films, a comprehensive understanding of the environmental influence in the process of thermal annealing is not achieved yet, as it is critically important to further improve the optoelectronic device performance. By taking advantage of synchrotron-based grazing incident wide-angle x-ray scattering (GIWAXS), we *in situ* monitor the transformation of organohalide perovskites from precursors to final films upon thermal annealing at different relative humidity. *In situ* GIWAXS reveals the formation of crystalline perovskite materials over relevant time and moisture scales to decipher the effect of humidity on both phase transition and crystal structures during annealing. These *in situ* measurements demonstrate that moderate humidity accelerates the formation of organohalide perovskites and improves the orientation of the film, but more than $50\%$ relative humidity retards the formation of perovskites and destructs their crystal structures. Furthermore, the highly orientated films obtained at optimized relative humidity are observed which could be attributed to the hydration of precursors. These findings clearly elucidate the influence of moisture environment in annealing process of organohalide perovskites and, in turn, allow us to correlate the improved performance of organohalide perovskite materials and devices to structural features in terms of environmental effects.

**10:00 AM BREAK**

**10:30 AM** ET05.07.07

**Advances in Perovskite Active Layer Stability**

Edward H. Sargent; University of Toronto, Toronto, Ontario, Canada.

I will discuss advances - including doping strategies and reduced-dimensional perovskites - in increasing the stability of the perovskite active layer.

**11:00 AM** ET05.07.08

**Dipolar Cations Confer Defect Tolerance in Wide Bandgap Perovskites**

Hairen Tan1, 2, Fanglin Che2, Mingyang Wei2 and Ted H. Sargent2; 1Nanjing University, Nanjing, China; 2University of Toronto, Toronto, Ontario, Canada.

Efficient wide-bandgap perovskite photovoltaics will enable tandem solar cells when successfully combined with low-bandgap absorbers such as crystalline silicon. However, wide-bandgap perovskite solar cells (PSCs) today exhibit performance far inferior to that of sub-1.6 eV bandgap PSCs. Their tendency to form a high density of deep-level trap states underpins this limitation. Here we show that healing the deep traps in mixed-cation-halide wide-bandgap perovskites – in effect, increasing the defect tolerance via cation engineering – could enable further performance improvements in PSCs. We achieve a stabilized power conversion efficiency (PCE) of $20.7\%$ for 1.65-eV-bandgap PSCs by incorporating a small concentration of dipolar cation additive. The devices exhibit a high open-circuit voltage ($V_{oc}$) of 1.22 V and a fill factor (FF) that exceeds 80%. We also achieve a PCE of 19.3\% for 1.1 cm$^2$ large-area devices with a $V_{oc}$ of 1.24 V. We achieved commensurable improvements in 1.74-eV-bandgap PSCs, where we obtained a stabilized PCE of 19.1\% together with a high $V_{oc}$ of 1.25 V and FF of over 80%. From density functional theory calculations, we find that the presence and reorientation of the dipolar cation in mixed perovskites can heal the defects that introduce deep trap states. Our findings shed light on defect healing in perovskite materials and pave the way to further increasing the efficiency of perovskite-enabled tandem photovoltaic devices.

**11:15 AM** ET05.07.09

**Degradation Analysis of Perovskite Films Using the Photo Thermal Induced Resonance Technique**

Hyang Mi Yu1, Hye Min Oh2 and Mun Seok Jeong1, 2; 1Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); 2Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Suwon, Korea (the Republic of).

Organic-inorganic mixed halide perovskite (MAPbX$_3$: MA=CH$_3$NH$_3^+$, X =Cl$^-$, Br$^-$, or I$^-$) are extensively used as absorbing materials for solar cell due to its broad absorption range and long charge carrier diffusion length. Despite its high photovoltaic efficiency, their poor stability remains a major challenge for high performance device and their commercialization. Perovskite films based on CH$_3$NH$_3$Pb$_{1-x}$Cs$_x$I$_3$ undergo rapid degradation when exposed to oxygen and moisture. To overcome this problem, many researchers have been studied about the degradation mechanism of perovskite films. However, these results were not simultaneously obtained with structural and chemical properties of perovskite films. Thus it is not provided complete degradation mechanism of perovskite films. In this work, we investigated the degradation mechanism of perovskite films by performing simultaneous measurement of the structural and chemical informations using the photo thermal induced resonance technique combined with atomic force microscope. Finally, this study will contribute to understanding of the mechanism of the degradation process of perovskite films and enhance the stability of perovskite optoelectronics field.

**11:30 AM** ET05.07.10

**First Principles Modelling of Grain Boundaries in (FA/Cs)Pb(I/Br) Perovskite Solar Absorbers**

Keith McKenna; Univ of York, York, York, United Kingdom.

Mixed-cation lead mixed-halide perovskite solar absorbers such as (FA/Cs)Pb(I/Br) exhibit remarkable and tunable optoelectronic properties that make them attractive for next generation solar cell technologies [1]. In practice such materials are always polycrystalline however the role of grain boundaries (GBs) remains poorly understood and a subject of much speculation. For example, separate experimental studies suggest GBs in MAPbI$_3$ can be both thermally and moisture stable and exhibit a tendency to form a high density of deep trap states underpins this limitation. Here we show that healing the deep traps in mixed-cation-halide wide-bandgap perovskites – in effect, increasing the defect tolerance via cation engineering – could enable further performance improvements in PSCs. We achieve a stabilized power conversion efficiency (PCE) of $20.7\%$ for 1.65-eV-bandgap PSCs by incorporating a small concentration of dipolar cation additive. The devices exhibit a high open-circuit voltage ($V_{oc}$) of 1.22 V and a fill factor (FF) that exceeds 80%. We also achieve a PCE of 19.3\% for 1.1 cm$^2$ large-area devices with a $V_{oc}$ of 1.24 V. We achieved commensurable improvements in 1.74-eV-bandgap PSCs, where we obtained a stabilized PCE of 19.1\% together with a high $V_{oc}$ of 1.25 V and FF of over 80%. From density functional theory calculations, we find that the presence and reorientation of the dipolar cation in mixed perovskites can heal the defects that introduce deep trap states. Our findings shed light on defect healing in perovskite materials and pave the way to further increasing the efficiency of perovskite-enabled tandem photovoltaic devices.

In this talk, I will present our recent theoretical predictions on the electronic properties of two types of GB in (FA/Cs)Pb(I/Br). We employ density functional theory methods similar to those we have previously applied to model extended defects in a range of other materials including CZTS, TiO$_2$ and Fe$_3$O$_4$. We find that for the $\Sigma 3$ (111) GB there is strong segregation of Br to the GB (but not Cs) and it remains electrically benign with no preferential electron or hole trapping. However, for the $\Sigma 3$ (112) GB there is strong segregation of both Cs and Br and this is associated with the introduction of shallow electron trap states at the GB. We note that this may be beneficial for efficient electron/hole separation since there is no tendency for holes to trap at the GB [9]. These results highlight the point that not all GB types are equivalent and so one needs to consider a range of GBs to build a statistical picture.
Importantly, mixed perovskite absorbers present the possibility of much wider compositional variations (even without intrinsic defects) and so understanding GB properties is key to understanding the behaviour of real polycrystalline materials.

[9] K. P. McKenna, manuscript in preparation

11:45 AM ET05.07.11
Divalent Anionic Doping in Perovskite Solar Cells for Enhanced Chemical Stability

Joe Gong1, Mengjin Yang3, Dominic Rebollar1,2, Peijun Guo3, Jordan Rucinski2, Zachary Liveris1, Richard D. Schaller1,4, Kai Zhu1 and Tao Xu1; 1Northern Illinois University, DeKalb, Illinois, United States; 2Argonne National Laboratory, Lemont, Illinois, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States; 4Chemistry, Northwestern University, Evanston, Illinois, United States.

Chemical stabilities of hybrid perovskite materials demand further improvement towards long-term and large-scale photovoltaic applications. Herein, we report enhanced chemical stability of CH3NH3PbI3 by doping divalent anion Se2- in the form of PbSe in precursor solutions to enhance the hydrogen-bonding-like interactions between organic cation and inorganic framework, as evidenced by redshifted N-H stretch from Fourier-transform infrared spectra. As a result, in 100% humidity at 40 °C, the 10% w/w PbSe-doped CH3NH3PbI3 films exhibited >140-fold stability improvement over pristine CH3NH3PbI3 films. Whilst perovskite film morphology of the PbSe-doped CH3NH3PbI3 films reserved, a top efficiency of 10.4% with 70% retention after 700 hours aging in ambient air was achieved on an unencapsulated 10% w/w PbSe:CH3NH3PbI3-based cell. Significantly, the incorporated Se2- effectively suppressed iodine diffusion in solar cell, leading to enhanced chemical stability of the silver electrodes. Successful doping of divalent Se2- in perovskite lattice is further confirmed by enlarged lattice spacing from X-ray diffraction patterns, asymmetric photoluminescence peaks with shoulder electronic states, and concomitantly increased electrical conductivity of 5%, 10% w/w PbSe:CH3NH3PbI3 thin films. This work could advance the fundamental understanding of degradation and stabilization of hybrid perovskites in both material and device settings.

SESSION ET05.08: Crystallization and Microstructure/Phase Control
Session Chairs: Joseph Berry and Ilaria Cianchetta
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room Ballroom B

1:30 PM ET05.08.01
Microstructural Tailoring of Pb-Based and Pb-Free Halide Perovskite Thin Films for Large-Area, Efficient and Stable Solar Cells

Nitin P. Padture; Brown University, Providence, Rhode Island, United States.

Solution-processed thin-film perovskite solar cells (PSCs), where the record efficiency has rocketed from ~4% to ~23% — comparable to commercial silicon-based solar cells — in just nine years, offer unprecedented promise of low-cost, high-efficiency renewable electricity generation. Organic-inorganic halide perovskites (OIHs) at the heart of PSCs have unique structures, which entail rotating organic cations inside inorganic cages, imparting them with desirable optical and electronic properties. To exploit these properties for PSCs application, the reliable deposition of high-quality OIH thin films over large areas is critically important. The microstructures and grain-boundary networks in the resulting polycrystalline OIH thin films are equally important as they control the PSC performance and stability. Fundamental phenomena pertaining to synthesis, crystallization, coarsening, microstructural evolution, and grain-boundary engineering involved in the processing of OIH thin films for PSCs will be discussed with specific examples. Additionally, the discovery of Pb-free, Ti-based all-inorganic halide perovskites will be presented, together with the demonstration of viable PSCs based on these new materials. The overall goal of our research is to have deterministic control over scalable processing of tailored halide perovskite thin films with desired compositions, microstructures, and grain-boundary networks for large-area, high-efficiency, and stable PSCs.

2:00 PM ET05.08.02
Combining In Situ Phase and Optical Characterizations to Unveil the Chemistry of CH3NH3PbI3 Formation

Tze-Bin Song1, Faizan Motiwala1,2, Megumi Mori1,2, Gideon Segov1,2, Camelia V. Stan3, Nobumichi Tamura4, and Carolin M. Sutter-Fella1; 1Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3University of California, Berkeley, California, United States; 4Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Over the past decade, organic-inorganic halide perovskite semiconductors have attracted substantial research attention for application in optoelectronic devices. The field is moving towards more and more complex chemical compositions enabling dramatically improved device performances. Those improvements however, were mostly achieved through empirical optimization of processing conditions. Due to the fast and complex chemical reactions of hybrid metal halide perovskites, significant variations in material properties and device performances are observed from previous reports. Therefore, in deep understanding of the fundamental film formation processes and relevant synthesis parameters is critical for the control of the final film properties and to achieve reproducible, high performance devices.

Here, we establish mechanistic insights into the film formation process of metal halide perovskites by developing complementary in-situ characterization techniques including synchrotron diffraction, optical imaging, and photoluminescence spectroscopy. These in-situ characterization techniques complement each other in providing a holistic picture of the relation between phase, optical response and morphology evolution. With our newly designed systems, we can provide real-time monitoring of thin film formation immediately after the spin-coating process which is commonly used in lab research. As a model system, we studied methylammonium lead iodide (CH3NH3PbI3) as one of the most studied compounds among organic-inorganic halide perovskites. At relevant time scales, we demonstrate how the precursor chemistry governs phase formation, crystallization kinetics, film morphology, and optical response. We find that the perovskite film morphology is directly related to the structure of the intermediate phase and by tuning the precursor...
chemistry, we are able to tune the film morphology. The precursor chemistry plays the main role in the perovskite film formation and prevents the formation of needle-like morphology. In addition, using the Cl chemistry, the disappearance and re-appearance of perovskite phases was observed over the course of crystallization which is distinctly different from other non-Cl chemistries. The combination of state-of-art in-situ characterization techniques could pave the way towards assessing the roles of synthesis and processing designs very efficiently thus, enables mechanistic insights and control of the film properties for high efficiency devices.

2:15 PM ET05.08.03
Adsorption Induced Anisotropic Growth—Band Gap Engineering in Gas induced Hybrid Perovskite
Savayantan Sasmal1, 2, Raj Pala2, Sri Sivakumar2 and Suresh Valiyaveettil1; 1National University of Singapore, Singapore, Singapore; 2IIT Kanpur, Kanpur, India.

Extremely high optical absorption, benign intrinsic defects, much longer diffusion length, a perfect synergy to achieve astonishingly high photovoltaic efficiency has made hybrid halide perovskites one of the major research fields in last few years. Additionally, facile band gap tuneability make this hybrid perovskites from the solvated intermediate and simultaneous relaxation of growth restriction on MAPbI3 during prolonged exposure of methylamine leading to structural transformation of sheet to particle with continuous band gap engineering reflected in continuous change in emissive properties. This selective adsorption induced anisotropic growth of MAPbI3 enable continuous shifting of conduction band of growing MAPbI3 proved by scanning tunnelling spectra was also validated by DFT simulation points to the partial charge transfer to nonbonding 6p orbitals of Pb responsible for tuning of band gap of MAPbI3. We believe this selective adsorption induced band gap tuning of MAPbI3 would encourage to prepare new series of variant of MAPbI3 which can be useful in tandem solar cell as well as light emitting diode and display application.

2:30 PM BREAK

3:30 PM ET05.08.04
Material Engineering for Wide-Bandgap Perovskite Solar Cells
Ni Zhao, Yang Zhou, Jie Cao and Ching-Ping Wong; Chinese University of Hong Kong, Shatin, Hong Kong.

Wide bandgap organic-inorganic hybrid perovskites with a bandgap ranging between 1.7-2.0 eV have shown great potential to improve the efficiency of single-junction silicon or thin-film solar cells by forming a tandem structure with one of these cells or with a narrow bandgap perovskite cell. However, solar cells based on this class of materials generally suffer from poor stability and a large open-circuit voltage (Voc) deficit, which is associated with the migration barriers in the lattice after the interstitial occupancy. Secondly, I will describe how improved grain crystallization and grain boundary passivation can be achieved simultaneously through tuning of perovskite precursor composition. Using FA0.17Cs0.83PbI3-xBrx (x=0.8, 1.2, 1.5 and 1.8) with a varied bandgap from 1.72eV to 1.93eV as the model system, we illustrate how precursor additive Pb(SCN)2 should be matched with a proper ratio of FAX (I and Br) to realize large grains with defect-healed grain boundaries. The optimized perovskite films showed good photostability at both room-temperature and elevated temperature. Moreover, the corresponding solar cells exhibited excellent photovoltaic performances with the champion Voc/stabilized power output efficiency reaching 1.244V/18.60%, 1.284V/16.51%, 1.290V/15.01% and 1.312V/14.35% for WB-OHIPS with x=0.8, 1.2, 1.5 and 1.8, respectively.

4:00 PM ET05.08.05
Homogeneity in Halide Perovskites—The Implications of Disorder on Stability and Advancing to a Terawatt Scale Photovoltaic Technology
Joseph J. Berry; National Renewable Energy Laboratory, Golden, Colorado, United States.

Photovoltaic devices based on hybrid organic-inorganic perovskite absorbers have reached outstanding performance over the past few years, surpassing power conversion efficiency of over 22%. This talk will discuss the progress at the National Renewable Energy Lab (NREL) on the challenges in hybrid perovskite solar cells (HPSCs) and stability of HPSC devices and materials. This talk will highlight work at NREL to develop understand and enhance stability of HPSCs. Discussion will focus on efforts to more carefully understand the implications of process on stability and efficiency in the HPSC devices. Connections to aspects of material formation and processing for high-volume manufacturing will also be made. In the case of stability, an examination of different perovskite active layers their formation and resulting interfacial electronic structure with contacts in the HPSCs stack will be presented. Work at NREL indicate interface formation of the active layer with different carrier transport materials has direct implications for performance and it evolution over time in the resulting devices will be built upon. Results extending these results to additional active layers and associated interfaces studies in which photomission, time resolved spectroscopy, structural studies and device level studies are combined indicates the importance of both processing and impacts of interface electronics and carrier dynamics. Results on the extension of existing stable architectures to mini-module devices will be presented along with performance data for these systems.

4:30 PM ET05.08.06
The Fluid Dynamics in Perovskite Scalable Coating and Its Suppression by Surfactants for Efficient Photovoltaic Modules
Yeheo Deng1, 2 and Jinsong Huang1, 2; 1University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 2University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Organic-inorganic hybrid perovskites are novel photovoltaic materials with high power conversion efficiency over 22% and low-cost solution processability. However, scaling up of perovskite fabrication remains a challenge due to the complex fluid dynamics within perovskite precursor solution when drying. Here, we show the fluid flow pattern observed by in-situ microscopy and report that surfactants additives can dramatically suppress the flow.
Two dimensional metal halide perovskites have demonstrated exceptional stability and performance in various optoelectronic applications. A key to their high performance is to align the insulating organic layers vertical to the substrates to avoid inhibition of charge transport. Several fabrication routes have been presented in literature but there is not yet a general strategy to orient 2D perovskite sheets vertically to the electrodes, due to lack of understanding of the crystallization process. In our research, based on our previous discovery that vertically oriented 2D perovskite crystallization can occur at liquid-air interface (Nature Communications 9, 1336 (2018)), we found that a low supersaturation during 2D perovskite crystallization is crucial for a strong degree of crystallographic orientation, confirmed by our in-situ grazing incidence X-ray diffraction measurement on thin films formed from different supersaturation environments. This understanding leads to a general strategy to fabricate vertically oriented 2D perovskite thin films through rational selection of solution formulation, organic spacers and processing conditions. It also allows control of the degree of orientation from complete random to complete vertical orientation. With this strategy we demonstrate vertically oriented thin films with various organic spacers and devices with high performance and long term stability.

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[1] Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D., Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California, United States.
[3] Anthopoulos1, Ioannis Spanopoulos1, Weijun Ke1, Constantinos Stoumpos1, Emily C. Schueller2, Oleg Kontsevoi1, Ram Seshadri2 and Mercouri G. Kanatzidis1; 1Northwestern University, Evanston, Illinois, United States; 2Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California, United States.

4:45 PM ET05.08.07
Alexander Z. Chen, Michelle Shiu, Mustafa Mahmoud, Xiaoyu Deng and Joshua Choi, University of Virginia, Charlottesville, Virginia, United States.

Two dimensional metal halide perovskites have demonstrated exceptional stability and performance in various optoelectronic applications. A key to their high performance is to align the insulating organic layers vertical to the substrates to avoid inhibition of charge transport. Several fabrication routes have been presented in literature but there is not yet a general strategy to orient 2D perovskite sheets vertically to the electrodes, due to lack of understanding of the crystallization process. In our research, based on our previous discovery that vertically oriented 2D perovskite crystallization can occur at liquid-air interface (Nature Communications 9, 1336 (2018)), we found that a low supersaturation during 2D perovskite crystallization is crucial for a strong degree of crystallographic orientation, confirmed by our in-situ grazing incidence X-ray diffraction measurement on thin films formed from different supersaturation environments. This understanding leads to a general strategy to fabricate vertically oriented 2D perovskite thin films through rational selection of solution formulation, organic spacers and processing conditions. It also allows control of the degree of orientation from complete random to complete vertical orientation. With this strategy we demonstrate vertically oriented thin films with various organic spacers and devices with high performance and long term stability.

SESSION ET05.09: Poster Session III: Fundamentals of Halide Perovskite Optoelectronics
Session Chair: Luis Ono
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Ilynes, Level 1, Hall B

ET05.09.01
Solution-Processed Mixed-Dimensional Hybrid Perovskite/Carbon Nanotube Layers and Their Application in Electronics
Chun Ma1, Sarah Clark2, Liangiang Liang1, Ran Tao1, Xinwei Guan1, Ali Han1, Xiaogang Liu1, Lian-Jong Li3, Mark C. Hersam2, Tom Wu1 and Thomas D. Anthopoulos1; 1KAUST, Thuwal, Jeddah, Saudi Arabia; 2Northwestern University, Chicago, Illinois, United States; 3National University of Singapore, Singapore, Singapore.

Organic-inorganic lead-based halide hybrid perovskite (PVK) have attracted tremendous attention in recent years because of their remarkable optoelectronic properties and their unprecedented potential in inexpensive photovoltaic (PV) applications. Despite the rapid progress in the PV sector, however, use of the technology in areas such as microelectronics, and particularly thin-film transistors (TFTs), has been plagued by relatively low carrier mobility, high threshold voltages and moderate channel current ON/OFF ratio. In this work, density gradient ultracentrifugation technique was used to first sort polychiral semiconducting single-walled carbon nanotubes (s-SWCNT), and secondly to incorporate them into mixed-cation perovskite (MA$_x$FA$_{1-x}$PbI$_3$Br$_{1-x}$)channel layers to produce TFTs with significantly enhanced performance characteristics. Optimised transistors are shown to combine low voltage operation (-1 V) with high carrier mobility (32.25 cm$^2$/Vs) and exceptionally high channel current channel ON/OFF ratio (10$^7$). The low threshold voltage and low sub-threshold slope (225 mV/dec) of the PVK/s-SWCNT-based TFTs enable the fabrication of high-performance inverters (NOT gates) and memristive transistors (memtransistors). Furthermore, temperature-dependent charge transport measurements reveal that the PVK/SWCNT-based TFTs undergo a change in the transport mechanism from ambipolar, in the high temperature range (300 – 160 K) to strictly unipolar at low temperatures (160 – 80 K), revealing the interplay of carrier injection, trapping and emission in such mixed-dimensional channels. The activation energy of holes was estimated to be 99.1 meV, highlighting the important role of defects in metal-halide perovskite materials. The combination of processing versatility, high charge carrier mobility, low-voltage operation and high current ON/OFF ratio highlight the potential of mixed-dimensional PVK/SWCNT systems for application in large-area microelectronics.

ET05.09.02
3D “Hollow” Hybrid Halide Perovskites—A New Platform of Light Absorbers
Ioannis Spanopoulos1, Weijun Ke1, Constantinos Stoumpos1, Emily C. Schueller2, Oleg Kontsevoi1, Ram Seshadri2 and Mercouri G. Kanatzidis1; 1Northwestern University, Evanston, Illinois, United States; 2Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California, United States.

Perovskite compounds exhibit exquisite electronic features for photovoltaic applications. Incorporation of those materials into solid state solar cells allowed the recording of very high power conversion efficiencies (PCEs) above 22%, which are comparable to the current commercial available materials[1]. However in order for perovskite compounds to reach eventually the market, some severe limitations have to be addressed. Those are not other than their inherent environmental instability and their composition of toxic elements (e.g. Pb$^2+$). In this work we address both those important issues by the discovery of a new family of 3D perovskites, namely “hollow” perovskites, with chemical formula (A)$_{1-x}(en)_x$(M)$_{1-0.7x}(I)_{3-0.4x}$, (A = methylammonium (MA), formamidinium (FA); M = Sn, Pb; en = ethylenediammonium) [2-4]. Incorporation of en cations in the 3D perovskite structure leads to massive M and I vacancies in the 3D [MA$_x$] framework, thus the term hollow. By adjusting the percentage of en in the structure we were able to fine tune the optical properties of the corresponding materials, maintaining at the same time the desired 3D structure dimensionality. These hollow perovskites exhibit significantly blue-shifted direct band gaps over a very wide energy range, from 1.25-1.51 eV for Sn-based perovskites and from 1.53-2.1 eV for the Pb-based analogues. DFT calculations revealed that as metal halide fragments are eliminated from the perovskite structure, the bands themselves become less disperse (i.e. narrower) due to the reduced lengths of fragments with M-I overlap. A most important outcome from this synthetic strategy is the superior enhancement of the air stability of the corresponding materials. The Sn based (MA$_{0.39}$(en)$_{0.6}$Sn$_{0.72}$(I)$_{2.84}$) perovskite is stable in air for at least 9 days, while the (FA)$_{0.6}$(en)$_{0.4}$(Pb)$_{0.3}$Sn$_{0.7}$(I)$_{2.44}$ perovskite is stable in air for more than 300 days. Both lifetimes are the highest reported for a 3D ASnX$_3$ and a 3D FAPbI$_3$ phase respectively. This family of perovskite compounds poses as a new platform of promising light absorbers that can be utilized in single junction or tandem solar cells.

References
ET05.09.03
Quasi-2D Ruddlesden-Popper Perovskite Blue Light-Emitting Diodes with Br-Based Mixed Spacers]

Recently, perovskite LED is attracting increasing attention as a next-generation LED that can replace existing OLED and QLED. However, methylammonium lead halide (MLH) based perovskites are not suitable for commercial application in LED devices due to its low stability against moisture. Recently, quasi-2D perovskites (PEA)2(MA)n-1PbnBr3n+1 have been reported to enhance the photoluminescence (PL) and water-stability compared to conventional MLH 3D perovskite (MAPbBr3). However, the development of conventional Ruddlesden-Popper phase perovskites has been only focused on green emission region. In this regard, herein we tried to tailor the emission range of Br-based quasi-2D perovskite from green to blue region by integrating organic cation spacers. As the candidates for the spacer, aromatic (phenylethylammonium (PEA), benzyltrimethylammonium (BTM)) and aliphatic (isopropylammonium (IPA), n-propylammonium (nPA)) cations were employed by controlling the relative concentration ratio. As a result, the PL intensities and the emission wavelength of the new class of quasi-2D perovskites, BTA and nPA-based perovskites, showed deep-blue emissions at 475 nm, with uniform and well-structured surface coverage. In addition, The PL intensity of the blue perovskite thin film was on par with that of the green one (((PEA)2(MA)n-1PbnBr3n+1). By controlling the ratio of BTA and nPA, we could fine-tune the PL wavelength from 610 nm (green) to 475 nm (blue) systematically (with 7 nm intervals). Based on our dimensionality-controlled perovskites, the blue-emissive Q-2D perovskite LED showed low turn-on voltage (less than 4 V) with high-current density (42 mA/cm2). The protocol and strategy established in this study can be exploited to enhance high-level electron quantum efficiency (EQE) and luminescence.

ET05.09.04
Highly Efficient Perovskite Quantum-Dot Light-Emitting Device by Gel Permeation Chromatography as New Purification Process and Interfacial Engineering Using Alkyl Ammonium Salt Layer

Lead halide perovskite (CsPbX3, X = Cl, Br, or I) quantum dots (QDs) have recently attracted considerable interest for light-emitting device (LED) applications such as thin film displays and solid-state lighting, owing to electroluminescence emission with narrow full width at half maximum (FWHM), tunable color properties by anion exchange method, and ease of solution processability (1,2). The optical properties of perovskite QDs as ionic nanocrystals are greatly affected by highly polar washing solvent due to occurring cation- and anion-defects (3). In this work, we achieved low driving voltage and high efficiency perovskite QD-LED using Gel permutation chromatography (GPC) with nonpolar solvent to remove excess ligand such as oleic acid (OA), oleylamine (OAM) and synthesize solvent 1-octadecene (ODE). We confirmed completely remove these impurities by GPC in contrast to conventional precipitation process. In addition, we demonstrated the effect of interfacial layer between the hole transport layer and the perovskite QDs by alkyl ammonium salts containing the Br anion, oleylamine bromide (OAM-Br) to passivate cation- and anion-defects. The LED based on OAM-Br interfacial layer exhibited higher efficiency compared to the LED without OAM-Br layer due to the suppression of interfacial cation- and anion-defects. Reference: (1) L. Protescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R.Caputo, C. H. Hendon, R. X. Yang, A. Walsh, and M. V. Kovalenko, Nano Lett., 2015, 15, 3692. (2) J. D. Roo, M. Ibanez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. V. Driesche, M. V. Kovalenko, and Z. Hens, Adv. Mater. 2016, 28, 8718. (3) T. Chiba, K. Hoshi, Y.-J. Pu, Y. Takeda, Y. Hayashi, S. Ohisa, S. Kawata, and J. Kido, ACS Appl. Mater. Interfaces, 2017, 9, 18054.

ET05.09.05
Metal Halide Perovskite Based Optical Phase Shifter—Giant Photocarrier-Induced Refractive Index Change

Metal halide perovskite are excellent optoelectronic materials that are quite suitable for thin-film solar cells, light-emitting diodes (LEDs), and lasers. This is because they exhibit strong optical absorption, high luminescence efficiencies, long carrier lifetimes, long diffusion lengths, and low densities of radiative recombination centers [1]. Recently, unique properties of halide perovskites have been discovered, e.g., photon recycling, ion migration, and local rearrangement of molecular dipoles [2-4]. These properties are expected to lead to the development of new-type optoelectronic devices. One of the most important properties of halide perovskites is that they crystallize in low-temperature solution processes. In particular, it is remarkable that large-size single crystals of halide perovskites can be grown in low-temperature solution exhibiting high optical transparency and exceptionally low surface light scattering. These optical properties are beneficial for novel optical transmission applications in the broad spectral range from visible to infrared. In this work, we studied the photocarrier-induced refractive index change in organic-inorganic hybrid perovskites. The crystal used in this study was a methylammonium lead bromide (MAPbBr3) single crystal. To measure the photorefractive properties of the halide perovskite, we developed an interferometric system that is synchronized with photoexcitation. The photorefractive phase shift was measured by detecting the phase shifts of the transmitted light through the perovskite single crystal mounted in the interferometric system. From the time-resolved measurements and excitation-pulse dependence of the photorefractive phase shifts, we clarified that photogenerated carriers cause extremely large and long-lived changes in the refractive index. This result shows that the perovskite single crystal works as an optical phase shifter. Moreover, we demonstrated that infrared laser light are tunable to any desired polarization configuration by employing the photorefractive phase shift. Our demonstrations provide new pathways to develop optical devices with organic-inorganic hybrid perovskites leading to variable wave plates, optical switches, and phase modulators. Part of this work was supported by JST-CREST (JPMJCR16N3) and JSPS KAKENHI (18K13481).


ET05.09.06
A Device Simulation of Organohalide Perovskite Resistive Random Access Memory

Resistive random access memory (ReRAM) based on organohalide perovskite (OHP) shows excellent properties compared to conventional metal oxide
resistive memory such as low operating voltage, high on/off ratio, and fast switching speed in several experimental demonstrations. Nevertheless, this technology is still in the premature stage. The design strategy of the active material and the device architecture must be established for the OHP ReRAM to be promoted to the stage of the commercial development. Thus, a device simulation based on finite element method is necessary to investigate the optimal device architecture on constituent materials and geometry. In this work, we will present a stochastic finite element simulation of conductive filament formation to perform reverse engineering on the material parameters of the OHP, in other words, to estimate which material parameters critically affect switching characteristics. In addition, the effects of device geometry and the nature of OHP/metal contacts were also studied.

ET05.09.07
First-Principles Investigations on Atomicistic Origin of I-V Hysteresis in Hybrid Perovskite Solar Cell Seong Hun Kim1, Pil-Ryung Cha2 and Donghwa Lee3; 1Pohang University of Science and Technology, Gyeongbuk, Korea (the Republic of); 2School of Advanced Materials Engineering, Kookmin University, Seoul, Korea (the Republic of).

In spite of the unprecedented advance of MAPbI3-based perovskite solar cell, there are still remaining issues to be resolved for its industrial applications. Especially, hysteresis in current-voltage (IV) curve is one of big challenges since it can limit its potential large scale application by causing abnormal efficiency drop. Various studies have proposed different physical origins such as ferroelectric polarization, charge trapping/detrapping and ion migration, none of study has clearly explained the microscopic origin of the hysteretic behavior in MAPbI3-based perovskite solar cell. In this study, thus we have employed first-principles density functional theory calculations to identify the atomicistic origin of hysteresis in MAPbI3. Our study has found that excess electrons or holes can stabilize two different iodine Frenkel defect structures in MAPbI3. Since excess charge carriers can be easily accumulated near the electrode interface, the formation of two different iodine Frenkel defects is inevitable and reversely it can act as a charge trap in MAPbI3-based solar cell. Thus, the hysteretic behavior of I-V curve is a result of charge trapping and detrapping during the formation of two types of iodine Frenkel defects near electrodes. Based on our understanding, we have suggested several possible ways to suppressed the hysteresis in MAPbI3-based solar cell.

ET05.09.08
Correlation between the Charge Transporting Layers and Defect States Distribution in Perovskite Solar Cells Measured by Admittance Spectroscopy Rasha A. Awwi, Changlei Wang, Xinxing Yan, Zhaoxing Song, Corey R. Grice, Lei Guan, Xiaoming Wang and Yanfa Yan; Department of Physics and Astronomy, and The Wright Center for Photovoltaics Innovation and Commercialization (PVIC), The University of Toledo, Toledo, Ohio, United States.

In the past decade, organic-inorganic halide perovskite solar cells (PVCs) have achieved outstanding progress in power conversion efficiency. However, solution-processed polycrystalline perovskite thin films possess a significant number of defects. Accurately probing the defect states distribution and understanding the origins of the defects are critical for further improving the device performance. Thermal admittance spectroscopy (AS) is a powerful characterization technique to determine the energetic distribution of trap states for different inorganic (e.g., CdTe, CuIn(Ga)Se2, etc.) and organic thin film solar cells, and has recently been used to characterize PVCs. Interestingly, some unique trap signatures were observed in the AS measurements of PVCs, but their origin has yet to be determined.

Here, we perform AS measurements on the PVSCs in the n-i-p planar structure to determine the impact of electron and hole transporting layers (ETL and HTL) on the trap states. We measured PVSCs with and without the SnO2/Cu2O-SAM ETL and the spiro-OMeTAD HTL as well as devices with different HTL thicknesses, doping densities, and materials. The AS measurements at different DC bias voltages are employed to identify where the trap features are originated from the bulk or interface defects. Our results show that defect states are less dependent on the ETL but strongly affected by the HTL. Additionally, we compared the admittance spectra of the n-i-p and p-i-n devices with the same absorber but different ETLs/HTLs. The devices exhibit different capacitance signatures, indicating that different states probe by AS are affected by the ETLs/HTLs. More importantly, we identify that the trap states that were originally attributed to perovskite absorber layer by previous studies may likely be originated from the spiro-OMeTAD HTL. Our approach provides insights on the defect state measurement using AS and the limitations of this method.

ET05.09.09
Impact of B-Site Doping on the Optical Properties of Lead Halide Perovskites Abdeljaleel Ismail, Mahesh K. Gangishetty and Dan Congreve; Rowland Harvard University, Cambridge, Massachusetts, United States.

Lead halide perovskites (ABX3) have been attractive materials for various applications in optoelectronics such as solar cells and light emitting diodes (LEDs). The quantum efficiency of green and red perovskite LEDs has reached over 10% within the last few years.1,2 The composition of the perovskite has been shown to play a crucial role on their optical properties. Recently, several groups including ours, found that doping the B cation site with Mn2+ can significantly improve photoluminescence quantum yields of perovskite quantum dots.3 In addition to the Mn2+, many other B cations have been suggested as potential dopants, however, only a few other cations have been studied in perovskites thus far.4 In this work, we explore the transport behavior and origins of the gas sensitivity in MAPbBr3 single crystals (SCs) devices using electrochemical impedance spectroscopy and current relaxation measurements. We show that the SC response to the environment is highly anisotropic and depends on crystal planes with respect to electrodes. Strong capacitive and resistive response occurs when crystals are exposed to N2 and O2. We discuss the possible interaction between N2 and O2 gases with the surface of MAPbBr3 perovskite SC. The observed behaviors suggest that the redox state of the
surface plays significant role in the transport phenomena but does not offer readily controlled redox environment. In addition, analysis of available data indicate that the response of MAPbI\textsubscript{3} SC is complex and likely related to volatilization process which can change the defect mechanisms and is highly localized on the surfaces and interfaces. The non-linear transport properties studied using pulse relaxation measurements in different environment. We notice that the potential drop across SC device is significantly higher in air as compare to N\textsubscript{2} and O\textsubscript{2} gases. The potential drop causes by space charges which screen the electric filed. The space charge is clearly affected by the environment. Next, we applied ultra-fast Kelvin Probe Force Microscopy to unravel spatio-temporal charge dynamics at SC/electrode interface for the first time. The relaxation processes observed in pulse relaxation and G-KPFM measurements along with gas sensitivity of crystals, suggests the presence of a triple phase boundary between electrode, and crystal. Results indicate that environment is a non-trivial component in the operation of OMHPs devices which is reminiscent of fuel cell systems. Furthermore, the triple phase boundary can play a significant role in the transport properties of OMHPs due to the possibility of the redox processes coupled to the concentration of bulk ionic species. While instrumental for understanding the device characteristics of perovskites, our studies suggest a new opportunity of coupling the redox chemistry of the Br\textsubscript{2}/Br\textsubscript{3} pair that defines the bulk conductivity of MAPbBr\textsubscript{3} with the redox chemistry of gaseous (or liquid) environment via a suitable electrocatalytic system to enable new class of light activated sensors and energy storage devices.

**ET05.09.11**

**Two-Dimensional Hybrid Perovskites for Tunable Energy Level Alignments and Photovoltaics**

Zhenyu Wang\textsuperscript{1,2,3}, Alex M. Ganose\textsuperscript{2,3,4}, Chuming Niu\textsuperscript{1} and David O. Scalon\textsuperscript{2,3,4}; \textsuperscript{1}School of Electrical Engineering, Xi’an Jiaotong University, Xi’an, China; \textsuperscript{2}Department of Chemistry, University College London, London, United Kingdom; \textsuperscript{3}Thomas Young Centre, University College London, London, United Kingdom; \textsuperscript{4}Diamond Light Source Ltd., Diamond House, Oxfordshire, United Kingdom.

Organic-inorganic lead halide perovskites have emerged as remarkable photovoltaic (PV) absorber materials in recent years. To date, polycrystalline thin-film perovskite photovoltaic devices have reached power conversion efficiencies reaching 22.7 \%. However, the involvement of a toxic element of lead and long-term instability are still the main issues in the large-scale commercial application of perovskites.

With excellent long-term durability and moisture tolerance, the possibility of flexible tuning of electronic properties, and coupled to low cost synthesis routes, the two dimensional (2D) hybrid halide perovskites have recently attracted much attention, and have been successfully used as light absorbers in efficient photovoltaic devices.\textsuperscript{2,3} 2D hybrid halides perovskites which feature long chain alkylammonium cations are generally suggested for light emitting diode applications, due to their strong photoluminescence (PL),\textsuperscript{4} but none have been applied thus far for photovoltaic applications. Additionally, the previous study has shown the luminescence quenching in the Pb-based analogues, (AEQT)PbX\textsubscript{4} (X = Cl, Br, I), the energy transfer and charge separation between organic and inorganic components of the structures are still not fully understood.\textsuperscript{4,5}

Herein, we investigate the geometrical, electronic and optical properties of the semiconducting 2D perovskites (AEQT)\textsubscript{2}M\textsubscript{8}X\textsubscript{4} (M = Sn, Pb, X = Cl, Br, I), using relativistic hybrid density functional theory calculations. We demonstrate that unlike the traditional 2D perovskites, the choice of the organic ammonium cation has a considerable effect on the carrier transport properties, and the energy transfer between the organic and inorganic components is symmetry-disallowed. The electronic structure of the series are flexibly tailored by different halides and metal cations, with band gaps from 2.06 to 2.68 eV. Unique energy level alignments greatly hinder the electron-hole recombination in (AEQT)PbCl\textsubscript{4}, (AEQT)PbBr\textsubscript{4}, (AEQT)PbI\textsubscript{4} and (AEQT)SnI\textsubscript{4}, and thereby enhance the PL efficiencies. With a moderate fundamental band gap (2.06 eV) and strong direct valence band to conduction band transition, (AEQT)SnI\textsubscript{4} is the only composition that shows intense and broad optical absorption, and as expect displays a high spectroscopic limited maximum efficiency (SLME) of 21.9 \%. Our results indicate the (AEQT)SnI\textsubscript{4} is a promising class of stable and efficient light-absorbing materials for photovoltaics.


**ET05.09.12**

**New Electron Transporting Materials for Perovskite LED**

Seokwoo Kang, Yeonhee Sim, Beomjin Kim and Jongwook Park; Kyung Hee University, Yongin, Korea (the Republic of).

In conventional organic light emitting diode (OLED), aluminium quinolone (Alq\textsubscript{3}) has been widely used as an electron transporting layer (ETL) in the past. And in the perovskite light emitting diode (pLED) device, \(1,3,5\)-tris(phenyl)-1-H-benimidazole (TPBi) has been generally used as an ETL because it has better ETL property based on the higher electron mobility than Alq\textsubscript{3} in the device. However, TPBi has disadvantage in terms of device life time compared to the Alq\textsubscript{3} because of the inferior thermal property. Therefore, we designed and synthesized new organic electron transporting materials for perovskite light emitting diode (pLED) which includes thiazolo[5,4-b]pyridine and benzo[h]quinolone moieties, respectively. We report the TPBi properties and long-term instability are still the main issues in the large-scale commercial application of perovskites.

In this work, pressure induced changes in the optical emission of two-dimensional perovskite crystals (PMAgPbI\textsubscript{4}) has been systematically studied at room temperature by various optical techniques, including photoluminescence (PL), time-resolved PL and Raman spectroscopy, all as a function of pressure. The crystals are pressurized inside a diamond anvil cell (DAC). At the pressure range of 0 to 3.5 GPa, the photoluminescence, originally at spectral position of \(-2.3\) eV, continuously shift to lower energies (red shift), and exhibits an ultra-wide tunable energy range of up to 350 meV spanning nearly the whole visible spectrum. Moreover, this energy tunability is fully reversible. In the used pressure range, the intensity of the emitted light is almost...
constant, while the PL lifetime keeps decreasing when increasing pressure, which implies that the efficiency of radiative recombination of excitons might be enhanced by pressure. First-principles simulations and X-ray diffraction (XRD) by synchrotron radiation both indicate that strong anisotropic compression along in-plane and out-plane directions should account for the red-shift of the band gap. Such a large optical tunability and constant emission quality within a relatively applied low pressure, has the potential to expand the applications of two-dimensional lead halide perovskite crystals in photonic and optoelectronic devices.


ET05.09.14 Sub-100nm Patterning of Perovskite Films by Self-Assembly of Block Copolymer Hyowon Han, Euihyuk Kim and Cheolmin Park; Department of Materials Science and Engineering, Yonsei University, Seoul, Korea (the Republic of).

While tremendous efforts have been made for developing thin organic lead halide perovskite films suitable for a variety of potential photovoltaic applications such as solar cells, field-effect transistors, and photodetectors, only a few works have focused on the micro or nanopatterning of perovskite films which is one of the most critical issues for large area, uniform micro or nanoarrays of perovskite-based devices. At present, patterning is only feasible at microscale, and at sub-100nm scale lithography of thin perovskite films has not yet been reported. Here, we demonstrate perovskite patterning at sub-100 nm scale without losing structural integrity and optical properties of the perovskite by an easy and simple method using self-assembly of the block copolymers. In order to make perovskite selectively segregated into one block, we utilized diblock copolymer, polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) consisting of non-interacting PS block and interacting Lewis base polymer P2VP block. By controlling the volume fraction (f_{PSVP}) and the amount of perovskite, the effective volume fraction (f_{PENC}) can be determined and various self-assembled nanostructures such as spheres, cylinders, lamellae can be successfully formed. The domain size of a perovskite crystal in the pattern could also be controlled by simply changing the molecular weight of the block copolymers. Our simple but highly controllable, nanopatterning of perovskites by self-assembly of block copolymers is promising and will enable applications of perovskite to highly integrated optoelectronic nanoscale devices.

ET05.09.15 Nanocrystallization and Optical Characterization of CH3NH3PbBr3 Perovskite via Ostwald Ripening Kazuki Umemoto1, Yuki Tezuka1, Tomoko Inose2, Hiroshi Uji-i2, Satoshi Asakura3 and Akito Masuhara1; 1Yamagata University, Yonezawa, Yamagata, Japan; 2Hokkaido University, Sapporo, Japan; 3ISE Chemicals Corporation, Tokyo, Japan.

Methylammonium lead halide perovskites have been applied to versatile applications owing to their attractive optoelectronic properties such as long carrier diffusion length, am-bipolar conductivity, broad color-tunable bath emission by halide ions. These potentials for applications with high performance are based on perovskite electro-optical features and they are expected to be used as next generation and solution processable semiconductor materials1. Recently, bright luminescence from methylammonium lead tri-chromide (MAPbI3) perovskite nanocrystals (PeNCs) has been reported owing to the development of methods for preparing these PeNCs. Especially, MAPbBr3 PeNCs were prepared by ligand-assisted reprecipitation2 (LARP) inspired by the precipitation method for preparing organic and nano/micro crystals. LARP can provide uniform MAPbBr3 PeNCs with narrow emission, which applies for successful implementation of PeNCs into LED.

Herein, we propose Ostwald ripening as a size-tunable technique for MAPbBr3 PeNCs using LARP. In a typical Ostwald ripening process, large crystals absorb solute from small ones in dispersion, as a result, large crystals grow bigger, and small crystals shrink. MAPbBr3 PeNCs could be size-controlled from several tens of nanometer size to 4 nm through shrinking of MAPbBr3 PeNCs and their PL peaks were consequently blue shifted from 514 nm to 457 nm. This suggests that Ostwald ripening can be expected to be an effective method for preparing PeNCs in the low nanometer size range.

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ET05.09.16 Efficient Upconversion Photoluminescence in All-Inorganic Perovskite Colloidal Semiconductor Nanocrystals Thu Ha T. Do, Andres T. Granados del Aguila, Jun Xing, Wen Jie Jee, Lulu Zhang and Qihua Xiong; Nanoyang Technical University, Singapore, Singapore.

Semiconductor colloidal nanocrystals (NCs) are efficient fluorescence emitters, whose emission wavelengths can be tuned by varying their sizes and chemical compositions. Recently, lead halide NCs with perovskite lattices have opened access to the deep-blue and green regions of the electromagnetic spectrum [1], where traditional II-VI nanocrystals such as the prototypical CdSe, undergo rapid degradation.

In this work, we investigate the optical properties of all-inorganic CsPbX3 (X = Cl, Br, I, ClBr4 and BrI4) perovskite nanocrystals. Specifically, we focus on their ability to convert low-energy into high-energy photons in a so-called upconversion photoluminescence (UCPL) process. Overall, all the investigated nanocrystals exhibit robust and efficient UCPL, characterized as a function of temperature, excitation energy and laser power. The UCPL phenomenon takes place in two distinguishable ways: (i) multiple-photon absorption and (ii) one-photon with the subsequent lattice vibrational (phonon) absorption. The latter mechanism demands an energy of up to 200 meV from the thermal bath, equivalently to the total energy of about ten optical phonons of CsPbX3 compounds. However, after the first few consecutive absorption steps, the finite optical phonon population in the nanocrystals would become deficient, therefore decreasing the UCPL efficiency. We argue that the annihilation of multiple low-energy phonons creates a high-energy vibration, which populates the optical phonon bath and consequently increases the light upconversion probability [2]. This energy recycling mechanism is particularly strong in semiconductors having low thermal conductivity, such as lead halide perovskites [3]. Our work explains for the outstanding laser cooling effect in these materials [4] and reveals the potential of high-quality CsPbX3 nanocrystals for several applications such as bioimaging, photovoltaic light-energy harvesting and optical refrigerators.

References
Research on lead halide semiconductors with perovskite lattices is a rapidly growing field in nanoscience and semiconductor physics. They have great potential for low-cost yet efficient solar cells and light-emitting devices [1,2]. Their optical properties can be tuned by tailoring the chemical composition and/or the nanostructure spatial dimension with very high precision and high quality. For example, the perovskite semiconductors can grow in stable layered structures, which comprise alternatively stacked layers of lead-halide octahedra and long-chain organic molecules. The inorganic framework, sandwiched between two organic layers, forms an atomically thin quantum well with macroscopic continuity.

Herein, we study the optical properties of high-quality two-dimensional (PEA)$_2$PbI$_4$ crystals. Four intrinsic optical transitions are resolved in the luminescence spectrum, originating from the radiative recombination of coupled electron-hole pairs (excitons) [3]. Intriguingly, the light emission is dominated by two excitons, each of which is split into two linearly polarized and orthogonal states. Their energy splitting is in the range of −1.2 meV, which is much larger than that of perovskite nanocrystals [4]. The highly anisotropic excitons may be resulted from the spin-orbit coupling and the exceptionally strong electron-hole exchange interaction. Moreover, at the low-energy side of the two doublets, we observe a feature arising from the recombination of a bright exciton. This line shows a circular dichroism, which can be induced either by circularly polarized excitation or by external magnetic field. This work is in line with the previous literature, where multiple excitonic features were resolved in bulk-like lead halide perovskites [5]. The observed energy landscape cannot be fully explained by available theoretical schemes for this material family. Our findings provide essential parameters for establishing a complete physical picture that governs the outstanding optical properties of two-dimensional layered perovskite semiconductors.

References


ET05.09.18

Volatility and Chain Length Interplay of In Situ Formed Primary Amines—Mechanistic Detail on Signal Transduction Properties of Hybrid Perovskites in Ammonia

Organic−inorganic halide perovskites, mainly known in photovoltaics possess promising signal transduction properties, which can be gainfully utilised in variety of sensing applications. Interestingly, highly polar nature of these class of materials, while being a bane in terms of stability, can be a boon for sensitivity while exposing with toxic gas like ammonia in a controlled atmosphere. This unusual signal transduction during sensing induces irreversible restructuring of perovskite crystal structure, which is one of the major lacuna preventing its utility in practical applications. To this end, we first elucidate the reasons behind the irreversibility of methylammonium lead iodide (MAPbI$_3$) associated with structural transformations and then developed a generic mechanistic route on interaction of ammonia (NH$_3$) with hybrid halide perovskite. The current investigation highlights that the vapor pressure of insitu formed alkylamine (due to facile proton exchange between alkylammonium cation present inside the hybrid perovskite crystal and approaching NH$_3$) determines the reversibility and stability of the original perovskite lattice. In addition, packing of alkyl ammonium chain inside the hybrid halide perovskite crystal provides accessible voids, which allows diffusion induced proton exchange reaction ultimately influence the rapidity of interaction with NH$_3$ gas. The mechanistic study addresses three important factors such as quick response, reversibility, and stability of perovskite materials in the presence of NH$_3$ gas, which could lead to the design of stable and sensitive two-dimensional hybrid perovskite materials for developing sensors.

ET05.09.19

Combinatorial Synthesis and PV Activity of Mixed A or X ABX$_3$ Halide Perovskites by Spray pyrolysis for Rapid and Systematic Parameter Space Mapping

Using ABX$_3$ Halide Perovskites, compositions with several monovalent cations occupying the A site and 2 types of halides the X site, in PV cells has yielded cell performances better than with one type of species on the A and X sites. Performance differences are not limited to conversion efficiency, but also to material and cell stabilities, under a variety of conditions. To date, reports on compositional changes have been limited to multiple single experiments that cannot cover all parameter space, which, strongly hinders mapping trends in compositions. This is where combinatorial materials science, CMS, and accompanying high-throughput analysis methods are important. In CMS compositional ranges can be prepared on a single substrate, making possible to do many experiments faster and in a comparatively more controlled manner. We report on CMS to form MAPbI$_3$($1_{1-x}$)$_{3_L}$, with systematically varying I and Br compositions to form a library of materials, using a home-built, controlled-environment tri-nozzle spray pyrolysis system. High-throughput optical characterization shows absorbance onset shifts of up to −150 nm depending on the composition (for MAPbI$_3$($1_{1-x}$)$_{3_L}$ in the range of x=0.2-0.8, as measured by EDS), allowing for fine-tuning of the bandgap along the library. X-ray diffraction showed peaks, corresponding for the perovskite structure, which, for the (220) one, range between $2\theta = 29.63^\circ$ - $30.02^\circ$, i.e., from the neat MAPbI$_3$ (220) towards 2$\theta =30.020$, which we ascribe to Br replacing some of the I. Also libraries where Cs (replacing the A cation), Rb (maybe interstitial) or both, were added, to yield MA$_x$Rb$_y$(PbI$_3$) , MA$_x$Cs$_y$(PbI$_3$), and MA$_x$Cs$_y$Rb$_z$(PbI$_3$) were synthesized. We will report on characteristics of both the films alone, and of PV cells with architecture FTO/ITO$_x$meso-TiO$_2$Halide Perovskite/Spiro-MeOTAD |Ag, and discuss trends observed for the different composition ranges, as trend identification is one of the most powerful ways to use CMS.

Reference:


ET05.09.20

Ambipolar Hybrid Perovskite Based Phototransistors Grown by Chemical Vapor Deposition

Low-cost hybrid organic-inorganic perovskites such as methylammonium lead iodide(MAPbI$_3$) have been developed intensively due to those high
absorption coefficient and easily tunable band gap, and easily fabricated by various deposition method such as solution-based process. However, solution-processed device using hybrid organic-inorganic perovskite is unstable and sensitive to water and ambient moisture. Therefore, the device stability is one of most important properties to achieve high performance hybrid organic-inorganic perovskite based devices.

In this paper, the electrical characteristics and stability of phototransistors using MAPbI₃, active layer were investigated. MAPbI₃ thin-film, prepared by chemical vapor deposition (CVD) with MAI and PbI₂ sources, and its physical, chemical, optical properties were compared with the solution-processed MAPbI₃ thin-film. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) revealed that solution-processed MAPbI₃ thin-film was easily transformed from MAPbI₃ to PbI₂ after 7 days later when exposed to air. However, CVD-grown MAPbI₃ thin-film showed great air stability maintaining its chemical composition and crystallinity above 1 month. Furthermore, atomic force microscopy (AFM) and scanning electron microscope (SEM) indicated that CVD-grown MAPbI₃ thin-film has large grain size and small surface roughness as compared to solution-processed MAPbI₃. MAPbI₃ phototransistor exhibits Insulating behavior in transfer characteristics, but ambipolar properties were observed when the visible light was irradiated. Finally, electrical stability such as negative bias stress (NBS), positive bias stress (PBS) of MAPbI₃ phototransistors were examined for the optoelectronic application.

ET05.09.21
Dipolar Disorder, Localized Charges and Their Effect on Charge Transport in Perovskites Ferdinand C. Grozema and Maria C. Gélvez-Rueda; Delft University of Technology, Delft, Netherlands.

A unique aspect of hybrid halide perovskite materials is the presence of an organic cation that occupies the cages formed by lead (Pb) and iodide (I). In the basic perovskite CH₃NH₃PbI₃, the methylammonium (MA) cation can rotate relatively freely, while slightly large cations can be restricted in their motion. Interestingly, the MA cation is dipolar and the organization of the dipoles in the material depends on the mutual interaction of the dipoles. It has been suggested that the formation of ordered domains can lead to electronic localized states that are different for electrons and holes, and therefore the dipolar disorder should influence the dynamics of charges formed on photo-excitation.

In this work we have performed a combined computational and experimental study to unravel the relation between dipolar disorder and charge dynamics. Using a combination of Monte Carlo simulations and classical molecular dynamics we have studied the dynamics of the MA dipole at different temperature and show that large ordered domains are formed at low temperature, while above a certain temperature the domains are very small and the dipole are rotation relatively freely. The temperature at which this transition occurs suggests that the phase transitions in the perovskite are induced by dipole alignment.

Subsequently, we have studied the effect of dipole orientation on the delocalization of electronic states in the material. It is shown that for organic cations with a relatively high dipole moment, such as MA, localized states are formed that are different for electrons and holes. For a low-dipole moment cation, formamidinium (FA) such localized states are not observed.

Finally, in order to gain insight in the effect of dipole motion on charge dynamics, we have performed time-resolved microwave conductivity measurements combined with generation of charges by irradiation with a short, high-energy electron pulse. We observe substantial changes in mobility and lifetime of charge carriers in CH₃NH₃PbI₃ after the low temperature tetragonal (β) to orthorhombic (γ) phase transition. We observed that the mobility and lifetime of charge carriers increase as the temperature decreases and a sudden increment is seen after the β/γ phase transition. For CH₃NH₃PbI₃ the mobility and the half-lifetime increase by a factor of three to six compared with the values before the β/γ phase transition. We attribute the considerable change in the dynamics at low temperature to the decrease of the inherent dynamic disorder of the organic cation (CH₃NH₃⁺) inside the perovskite crystal structure. When replacing the dipolar MA cation by FA such sudden changes in the charge dynamics are not observed. This indicates that the dipolar motion of the organic cation does influence the dynamics of charges, particularly at lower temperature.

ET05.09.22
Towards Stable Deep-Blue Luminescent Colloidal Lead Halide Perovskite Nanoplatelets—Systematic Photostability Investigation Seung Kwon Ha, Catherine M. Mauck and William Tisdale; Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recently, colloidal lead halide perovskite nanoplatelets have emerged as promising semiconductor materials due to their exciting properties such as tunability, facile processability, and high brightness with high color purity. In particular, their quantum-dielectric-confined nature makes colloidal lead halide perovskite nanoplatelets a favorable candidate for the next-generation deep-blue-emitting (475 nm) material platform. However, for light-emitting applications, poor photostability is one of the critical challenges that those nanoplatelets face. When exposed to UV excitation, they either suffer from photobleaching or transform into thicker—more bulk-like—structures with red-shifted emission.

In this study, we systematically investigate the factors that affect the photostability of the deep-blue-emitting perovskite nanoplatelets by monitoring the photoluminescence and absorption spectra over time. We find that freshness of the precursor solution for ligand-assisted reprecipitation is critical to obtain better stability with high photoluminescence quantum yield of perovskite nanoplatelets. Also, photobleaching is found to be the sign of intrinsic instability in nanoplatelets while transformation represents an extrinsic instability. Importantly, moisture is identified as the key extrinsic factor responsible for the transformation of nanoplatelets into more bulk-like structures. Furthermore, we observe that the substitution of the organic cation from formamidinium to methylammonium and addition of excess ligands significantly enhances the intrinsic stability of perovskite nanoplatelets. Lastly, we demonstrate that the dropcasted film of methylammonium-based nanoplatelets with excess ligands is impressively stable under ambient conditions and does not transform even under intense UV in the presence of moisture, as a result of improved intrinsic stability. This study expands our understanding of the factors that affect perovskite nanoplatelet photostability and opens up new possibilities for fabrication of stable perovskite-nanoplatelet-based optoelectronic devices with enhanced stability.

ET05.09.23
Anion Exchange Perovskite Quantum Dots for Highly Efficient Light-Emitting-Devices Takayuki Chiba, Yuukihiro Hayashi, Hinako Ebe, Satoru Ohisa and Junji Kido; Yamagata Univ, Yonanawa, Japan.

All-inorganic cesium lead halide perovskites quantum dots (QDs), CsPbX₃ (X = Cl, Br, I), have recently attracted much attention for use in light emitting devices (LEDs), given their high colour purity and narrow full width at half maximum (FWHM) over the entire visible wavelength range as well as their low-cost solution processing (1, 2). Here, we demonstrate unambiguous evidence that anion exchange QDs CsPbBr₃, using ammonium iodide salts, long alkyl based oleylammonium iodide (OAMI) and ary1 based aniline hydroiodide (AnHI), for use in highly efficient LEDs. The ester solvent ethyl acetate, which has a low dielectric constant, is used as poor solvent in reprecipitation process to remove impurities and prevent surface defects in the perovskite QDs. The anion exchange CsPb(Br/I)₃ films exhibit a strong red shift in their of photoluminescence (PL) spectrum from the green emission at 508 nm in the case of the pristine QDs to one in the deep-red region at 649 nm owing to the replacement of Br anions by I anions in the perovskite QDs. The anion exchange CsPb(Br/I)₃ film based on OAMI shows a high surface coverage ratio and is free of pinholes, whereas that of AnHI based CsPb(Br/I)₃ exhibits a slightly rough surface owing to a reduction in the surface ligand, which results in the aggregation of the QDs. LEDs formed using
the anion-exchange CaPb(Br/I), based on OAMI show an remarkable high EQE of more than 20% as well as high color purity, with the Commission Internationale de l’Eclairage (CIE) at (0.72, 0.28), which completely cover BT2020 color gamut. Similarly, the LEDs formed using the QDs based on AnHl show a peak EQE of 14.1% and CIE coordinates of (0.71, 0.28). Further, they exhibit longer operational stability as compared to that of LEDs formed using the OAMI based CaPb(Br/I).

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ET05.09.24
What Limits the V_{OC} of Br-Based Perovskite Solar Devices? David Cahen1, Arava Zohar2, Michael Kulbak1, Igal Levine1, Gary Hodes1 and Antoine Kahn1; 1Weizmann Institute of Science, Rehovot, Israel; 2Princeton University, New Jersey, Idaho, United States.

Thanks to the efforts of many research groups worldwide in halide perovskite (HP) research, >22 % efficient small photovoltaic (PV) devices have been reported [1]. Such devices, based on HaPs with mostly iodide as halide, can show a remarkably low voltage loss (E_{G}-V_{OC}) of ~0.4 V. Unfortunately, up to now, for the higher bandgap HaPs, where the halide is only Br, the highest reported V_{OC} still leaves (E_{G}-V_{OC}) ~0.75 V [2]. This large loss severely detracts from the potential of HaPs that have enough Br substitution for I, for optimal use in the higher E_G-based cell for tandem configurations or spectral splitting systems. The origin of this increased loss remains an open question.

Here we used (FM0.85MA0.1Cs0.05)PbBr3 (from hereon mixed-cation) as the photo-absorber. Previously we showed that this mixed-cation HaP has relatively long carrier diffusion lengths and low carrier density compared to single cation Br-based HaPs, more resembling the I-based HaPs, with which the small (E_{G}-V_{OC}) cells can be made.[1]

By using optoelectronic measurements such as Contact Potential Difference, Surface Photovoltage, Electroluminescence and Capacitance Voltage on mixed cation Br-based HP stand-alone films, as well as in different device configurations, we can now provide insights into the origins of the large (E_{G}-V_{OC}) for the BR-based HaP-based PV cells and suggest how these losses may be minimized.

Several discussions with Dr. Davide Cerutti (WIS) and Prof. Antoine Kahn (Princeton U) are gratefully acknowledged.

Reference
Metal halide perovskites (MHP) are promising next-generation materials for use in lightweight, flexible and inexpensive solar cells with power conversion efficiencies rivaling that of commercial silicon solar cells. The two main classes of MHP, hybrid organic-inorganic and fully inorganic, are hotly debated in the field as to which will become the commercially viable composition of MHP. Hybrid organic-inorganic perovskites have demonstrated high solar cell efficiency but relatively poor stability whereas fully inorganic MHPs are more stable with significantly lower solar cell efficiency. Therefore, it is important to understand whether or not organic cations play any roles in high solar cell efficiency so that the field can rationally decide which compositions to focus on for future development. Here we report our studies on the effect of cation composition on charge carrier recombination dynamics. Through a combination of novel ion exchange procedure, intensity dependent time-resolved photoluminescence (ID-TRPL) and transient absorbance (TA), the recombination rate constants were determined from systematically tuned compositions of various MHP thin films. Our results show that the choice of organic cations has a major influence in determining charge carrier recombination dynamics. Implication of these results on selecting optimum compositions for higher solar cell efficiency and stability will be discussed.

**ET05.09.27**

**Choice of Monovalent Cations Has Major Impact on Charge Carrier Recombination in Metal Halide Perovskites**

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Organic-metal-halide perovskite materials recently attracted immense attention due to its unique optoelectronic properties, easy and versatile synthesis routes and its applicability in photovoltaic and light emitting devices. The existing literature demonstrates that the device performances depend heavily on the film morphology, shape and size of the crystal and of course the stoichiometry of the synthesized material. In this presentation, I will be discussing some interesting and unique optoelectronic properties of some “bad” perovskite materials when it is either synthesized under non-ideal conditions or as non-stoichiometric which is not ideal for high performance devices. Here I will aim to justify a distinct correlation between the surrounding ambient and the PL intermittency of isolated and conjugated formamidinium lead bromide (FAPbBr3) microcrystals having dimension higher than the excited carrier diffusion length. A custom-built spectrally resolved epi-fluorescence microscopy is used to capture the wide-field optical emission properties of the material. With adequate experiments, we are able to describe the role of photoelectrochemically generated trap states that plays a deterministic role in PL intermittency. We further aim to establish a direct correspondence between the material degradation and the blinking.

**Figure 1:** Shows the photoluminescence intermittency in the FAPbBr3 microparticle

**ET05.09.28**

**Photoluminescence Intermittency in Micron-Size Hybrid Lead Halide Perovskites**

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Organic-metal-halide perovskite materials has been emerged as promising cost-effective and highly efficient nanostructured solar cells. The organometallic halide perovskite (PSCs) has recently emerged as promising cost-effective and highly efficient nanostructured solar cells. The organometallic halide perovskite such as CH3NH3PbI3 has poor thermal and air stability. To avoid this problem, there are many researchers who used the three-dimensional-type perovskite crystal structure with mixed cation such as cesium (Cs) and methyl amine (MA). The mixed cation perovskite has reported high thermal stability with improvement of the power conversion efficiency (PCE). The inorganic cesium lead iodide perovskite (CsPbI3) has been reported to have highly efficient optical properties and electrical properties. It should also be noted that the reported CsPbI3 perovskite solar cells with high efficiency has CsPbI3 in X-ray diffraction (XRD) measurement. In this study, we replaced MA with Cs and used vacuum deposition method to yield efficient inorganic planar heterojunction CsPbI3 solar cells. The CsPbI3 perovskite layer was formed by vacuum deposition of lead iodide (PbI2) and cesium iodide (CsI). The perovskite stoichiometry depends on the ratio of CsI and PbI2. The ratio of the codeposition rates of PbI2 and CsI was adjusted to PbI2/CsI of 1 to 3. The pure CsPbI3 film has a power conversion efficiency of 5.71%, leading to PCE of 3.77%. These results indicated the effect of Cs4PbI6 to improve the solar cell performance of Voc and FF in CsPbI3 based perovskite solar cells.

**ET05.09.29**

**The Formation of Cs4PbI6 and Its Effect for Device Characteristics in CsPbI3 Based Perovskite Solar Cells**

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Organometallic halide perovskite (PSCs) has recently emerged as promising cost-effective and highly efficient nanostructured solar cells. The organometallic halide perovskite such as CH3NH3PbI3 has poor thermal and air stability. To avoid this problem, there are many researchers who used the three-dimensional-type perovskite crystal structure with mixed cation such as cesium (Cs) and methyl amine (MA). The mixed cation perovskite has reported high thermal stability with improvement of the power conversion efficiency (PCE). The inorganic cesium lead iodide perovskite (CsPbI3) has been reported to have highly efficient optical properties and electrical properties. It should also be noted that the reported CsPbI3 perovskite solar cells with high efficiency has CsPbI3 in X-ray diffraction (XRD) measurement. In this study, we replaced MA with Cs and used vacuum deposition method to yield efficient inorganic planar heterojunction CsPbI3 solar cells. The CsPbI3 perovskite layer was formed by vacuum deposition of lead iodide (PbI2) and cesium iodide (CsI). The perovskite stoichiometry depends on the ratio of CsI and PbI2. The ratio of the codeposition rates of PbI2 and CsI was adjusted to PbI2/CsI molar ratio. The CsPbI3 film has a power conversion efficiency of 5.71%, leading to PCE of CsPbI3. In this case, a power conversion efficiency of 5.71% was obtained with a short-circuit current density (Jsc) of 13.50 mA/cm2, open-circuit voltage (Voc) of 0.55 V, and a fill factor (FF) of 0.51. This ideal film has not only CsPbI3 but also Cs4PbI6 was observed by XRD measurement. The Cs4PbI6 was considered to be the constituent of 3CsI and PbI2. To obtain the pure CsPbI3 perovskite film, we controlled the PbI2/CsI molar ratio of 1 to 3. The pure CsPbI3 perovskite film has a power conversion efficiency of 5.71%, leading to PCE of 3.77%. These results indicated the effect of Cs4PbI6 to improve the solar cell performance of Voc and FF in CsPbI3 based perovskite solar cells.

**ET05.09.30**

**Revealing the Relationship Between Structure and Opto-Electronic Properties of the Double Perovskite PV Candidate Cs2AgBiBr6**

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The discovery of hybrid halide perovskites materials heralded a new era in optoelectronic technologies, with an unprecedented rise to above 20% in the efficiencies of photovoltaic devices in just a few years. However, several crucial issues, such as stability and toxicity, still need to be tackled before an industrial-scale use. Although the presence of Pb in archetypal perovskites is unlikely to be a barrier or pose any considerable environmental risk for use in PV electricity generation, Pb may prevent use in certain applications such as bioelectronics and consumer electronics products. Therefore, several effort has been put in the research of a lead-free, stable all inorganic compound with improved thermal stability.

Recently, a new class of candidate photovoltaic materials – the double halide perovskites with chemical formula A2B8X6 (A, B=monovalent

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Here, we present a case study of a PSC based on a new compound material (MA0.6FA0.4PbI2.8Br0.2) that does not show a phase transition for relevant negative loops that appear in the medium and low frequency ranges further complicate a straight interpretation of the impedance response of PSC. The bismuth based perovskites are low-toxic and air stable materials with promising photo-absorber properties. The detailed studies on these materials are important for further development of solar cells. In this work, we have fabricated the Bi-based perovskite materials (Cs3Bi2I9, CsBi3I10) by solution process started to appear in the literature, yet very little is known about the relationship between the crystal structure and the opto-electronic properties of this mixed crystalline phase are speculated to be deleterious for getting efficient solar cell device.

Investigation of Bismuth Based Perovskite Thin Film for Solar Cell Application

The bismuth based perovskites are low-toxic and air stable materials with promising photo-absorber properties. The detailed studies on these materials are important for further development of solar cells. In this work, we have fabricated the Bi-based perovskite materials (Cs3Bi2I9, CsBi3I10) by solution process and investigated the crystal growth and optoelectronic properties of those materials. The XRD patterns of those materials suggest a hexagonal crystalline phase having different dominating diffraction peaks. The crystal quality is found to be affected by stoichiometric and growth temperature. The optophysical properties show a bandgap of ~2.1 eV for Cs3Bi2I9 thin film whereas it is quite smaller for the CsBi3I10 thin film (~1.75 eV). A device efficiency of over 1% is achieved for Bi-based perovskite device. Although the Bi-based perovskites are stable under ambient air, the poor film morphology and mixed crystalline phase are speculated to be deleterious for getting efficient solar cell device.

Photoelectrochemical Impedance Measurements on Perovskite Solar Cells with Improved Thermal Stability

Recently, electrochemical impedance spectroscopy (EIS) on perovskite solar cells (PSC) has gained a lot of interest in the literature. The time constants are on a favorable timescale to enable high quality EIS measurements and the cells have become stable enough to allow for reliable and reproducible measurement results, making EIS a most promising tool for characterization and diagnosis of PSC. Here, we present a case study of a PSC based on a new compound material (MA2-xFAxPbI3-xBrx) that does not show a phase transition for relevant ambient conditions and has proven to exhibit better thermodynamic stability than standard MAPbI3. Measurements were conducted on samples based on either of these materials. Fresh samples as well as samples that have been subjected to a temperature treatment beyond the MAPbI3 phase transition temperature of 328 K were used. All cells were characterized by EIS and intensity modulated photocurrent-voltage spectroscopy (IMPS/IMVS). IMPS is usually only measured under short circuit conditions (SCC) and IMVS only under open circuit conditions (OCC). In contrast to this practice, we have measured EIS, IMPS and IMVS at various potentials including OCC and at different light intensities. We show that the three measurement techniques form a triplet where one of them can be calculated with good accuracy if the other two are available.

As a result of this study, we will show how impedance measurement under open circuit conditions (OCC) can help to distinguish between different mechanisms but are less sensitive to device degradation. Measurements at a voltage range between 0 Volts and OCC can help to quantify degradation, which is represented by a decrease in the impedance at voltages below the maximum power point (MPP) and by an increase beyond the MPP.

The similarity of EIS and IMVS results has been discussed in the literature. We will argue and demonstrate how a comparison of EIS and IMVS can help to distinguish between interface effects and the behavior of the bulk photovoltaic layers. This contribution will be complemented by a few practical guidelines for reliable photoelectrochemical impedance measurements, as this comprehensive study was performed on some of the most stable PSC for which a degradation of less than 20% after 500 hours has been demonstrated, even at an elevated temperature of 85°C.

Chemical Nature of Ferroelastic Twin Domains in CH3NH3PbI3

Recently, observations of twin domain in methylammonium lead triiodide (MAPbI3) have drawn significant attention. However, whether this twin domain is ferroelectric and/or ferroelastic remains unclear. In addition, previous investigations were limited to the ferroic properties of this twin domain, whereas, the chemical behavior which can correlate with either ferroelectricity or ferroelasticity, has rarely been studied. In this work, we unveil the correlation of ferroelastic domains and chemical variation in the MAPbI3 twin domains using multiple functional imaging techniques. We unambiguously show the chemical origin of piezoelectric-like contrast by using multiple advanced piezoresponse force microscopy techniques, suggesting the non-ferroelectricity of this twin domain. The combination of helium ion microscopy secondary ion mass spectroscopy (HI-MSIMS) and nanoscale infrared spectroscopy
Furthermore, we found that two independent trion generation pathways exist by analyzing the excitation power dependence of trion components. We suppressed by the surface treatment as observed the difference in excitation power dependence, while exciton and biexciton components exhibit the same.

and untreated samples. We analyzed the excitation power dependence of the differential TA signals for each sample, and compared the extracted nonlinear optical response of the material also becomes more crucial. However the nonlinear optical responses in MAPbCl3 are less explored. With this in

In this work, we investigated the trion generation dynamics by modifying the surface state of cesium lead halide perovskite CsPbBr3 NCs. Femtosecond transient absorption (TA) spectroscopy was employed to investigate the ultrafast carrier dynamics in these NCs. The sample used in this experiment was a solution of the NCs dispersed in octane. We used sodium thiocyanate (NaSCN) as a capping (surface-modifying) ligand and prepared both surface-treated and untreated samples. We analyzed the excitation power dependence of the differential TA signals for each sample, and compared the extracted components of excitons, trions, and biexcitons between the surface-treated and untreated samples. We clarified that the generation of trions are clearly suppressed by the surface treatment as observed the difference in excitation power dependence, while exciton and biexciton components exhibit the same. Furthermore, we found that two independent trion generation pathways exist by analyzing the excitation power dependence of trion components. We discuss the trion generation dynamics in CsPbBr3 NCs from the viewpoints of extrinsic surface traps and intrinsic Auger recombination.

Part of this work was supported by JST-CREST (JPMJCR16N3).


Gram-Scale Synthesis of All-Inorganic Perovskite Quantum Dots with High Mn Substitution Ratio and Enhanced Dual-Color Emission

Mn-doped all-inorganic perovskite quantum dots (QDs) provide prominent applications in the fields of low-cost light source or LEDs, because of their remarkable properties including dual-color emission and reduced lead content, as well as high photoluminescence quantum yields (PLQYs) and high stability. The real dual-color emission with two strong emission peaks in individual crystals is particularly promising in the application of white LEDs. However, the existing approaches for synthesis of all-inorganic perovskite QDs with real dual-color emission and high Mn substitution ratio usually require harsh conditions, such as high temperature and nitrogen protection, which is a major hurdle for the practical manufacturing. Here we present a gram-scale approach to synthesize both CsPbMn1-xCln-xBr3 and CsPb1-xMnxCl1-xBr3 QDs at 100°C in the air with high Mn substitution ratio, up to 53.64% atomically. The as-prepared CsPbMn1-xCln-xBr3 QDs exhibit high PLQYs of 62.41% and dual-color emission with two strong emission peaks around at 400 - 460 nm and 600 nm, respectively. Furthermore, the unique advantage of the optical emission and high PLQYs properties of the CsPbMn1-xCln-xBr3 QDs has been demonstrated as invisible ink for encryption application and polymer composites. Our gram-scale synthesis approach for Mn-doped all-inorganic perovskite QDs may boost the future research and practical application of QDs-based white LED, spintronics, and molecular barcoding.

Understanding Effects ofPrecursor Solution Aging in Triple Cation Lead Perovskite

Solution process is the most widely used method to prepare perovskite absorbers for high performance solar cells due to its ease of fabrication and low capital cost. However, an insufficient level of reproducibility of the solution process is often a concern. Complex precursor solution chemistry is likely one of the main reasons for the reproducibility issue. Here we report the effects of triple cation lead mixed-halide perovskite precursor solution aging on the quality of the resulting films and the device performance. Our study revealed that precursor solution aging has a great influence on the colloidal size distribution of the solution, which then affects the phase purity of the films and device efficiency. We determined the optimum aging hours that led to the best device efficiency along with the highest reproducibility. Dynamic light scattering revealed the formation of micron-sized colloidal intermediates in the solution when aged longer than the optimum hours and further analysis along with X-ray diffraction measurements suggested there were two chemical origins of the large aggregates, FA-based and Cs-based complexes.

Nonlinear Optical Properties of MAPbCl3 Perovskite Single Crystals

Lead-halide perovskite semiconductors MAPbX3 (MA = CH3NH3, X = I, Br, and Cl) attract attention as a new class of photonic device materials [1]. The energy conversion efficiency of MAPbI3 thin-film solar cells has been improved rapidly and is now reaching to 22.7%. The sharp optical absorption edge and high-efficient band-to-band light emission of perovskites are the key factors for such high conversion efficiency. Due to these superior optical properties, a unique phenomenon of repeated photon emission and reabsorption, so-called photon recycling, appears remarkably in perovskite single crystals [2-4].

A wide bandgap perovskite MAPbCl3 is attractive for optical devices in blue spectral region. Particularly, for laser and optical switch applications, a nonlinear optical response of the material also becomes more crucial. However the nonlinear optical responses in MAPbCl3 are less explored. With this in mind, we conducted the measurements to obtain the nonlinear refractive index and nonlinear absorption coefficient for the wide wavelength range. Thin-film perovskite samples are usually influenced by the polycrystalline grain structure, making it difficult to measure intrinsic properties [1]. Thus, we
employed perovskite single crystals in order to eliminate such influences and determine the nonlinear optical coefficients.

The polycrystalline samples used in this study were prepared by antisolvent vapor diffusion method. The nonlinear refractive index and nonlinear absorption coefficient were determined by performing Z-Scan method with variable incident laser intensity. Moreover, the wavelength dependence of the nonlinear optical coefficient was measured by changing the incident laser wavelength. Furthermore, we measured two-photon photoluminescence excitation (PLE) spectrum of MAPbCl₃. The wavelength dependence of the nonlinear absorption coefficient can also be obtained from the two-photon PLE spectrum. We observed the trend that the nonlinear absorption coefficient increases at shorter wavelengths [5]. Our results contribute to understanding the nonlinear optical properties of the lead-halide perovskites and lead to advanced optical applications.

Part of this work was supported by JST-CREST (JPMJCR16N3).


SESSION ET05.10: Composition Tuning in Perovskites—Lead-Free Perovskites, Low-Dimensional Perovskites and Perovskite Alloys
Session Chairs: Shuji Hayase and Qing Shen
Thursday Morning, November 29, 2018
Hynes, Level 3, Room Ballroom B

8:00 AM ET05.10.01
Zero-Dimensional Organic-Inorganic Perovskite Variant—Transition Between Molecular and Solid Crystal Minggang Ju and Xiao Cheng Zeng; Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

Low-dimensional organic-inorganic halide perovskites (OIHPs) have attracted intense interests recently for photovoltaic applications, owing to their markedly high chemical stability compared to the widely studied three-dimensional (3D) counterparts. However, low-dimensional OIHPs usually give much lower device performance than the 3D OIHPs. In particular, for the zero-dimensional (0-D) OIHPs, it is believed that the strong intrinsic quantum-confinement effects can lead to extremely low carrier motility which severely limit the photovoltaic performance. Herein, we predict a new family of 0-D perovskite variants that, surprisingly, exhibit outstanding optoelectronic properties. We find that some compounds based on V exhibit typical features of 0-D perovskites, such as low carrier mobilities and strong quantum confinement, thereby limiting their applications in optoelectronic devices. Sb and Bi based 0-D perovskites possess features of molecular crystal, such as comparable absorption spectrum of sun light, and carrier mobilities for PV application. The unique properties are due to the CBM shows strong hybrid state between Sb 5s orbital and Br 4p orbital in ASbBr₆, and the hybrid states have strong overlap among neighboring octahedrons. Moreover, the bandgap can be tuned over a wide range via tuning the composition in the mixing element strategy. The newly obtained insight into unique optoelectronic property of the 0-D perovskites offers a rational design strategy for low-dimensional perovskites to address some known challenging issues inherent in the lead halide perovskite solar cells.

8:15 AM ET05.10.02
Optical and X-Ray Spectroscopy of the Ruddlesden-Popper Perovskite Sulfides Shanyuan Niu1, Debarghya Sarkar2, Kristopher Williams3, Kevin Ye4, Yuwei Li5, Elisabeth Bianco6, Wei Li7, Michael McConney8, Ralf Haiges9, Anderson Janotti7, David Singh5, William Tisdale3, Rafael Jaramillo4, Rehan Kapadia2 and Jayakanth Ravichandran1; 1Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States; 2Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California, United States; 3Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, United States; 5Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri, United States; 6Department of Chemistry, Rice University, Houston, Texas, United States; 7Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, United States; 8Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States; 9Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California, United States.

Transition metal perovskite chalcogenides are promising materials for photovoltaic applications with excellent optoelectronic properties, stability, and rich tunability. Recent experimental studies have revealed their promising potential, including band gap tunability all the way from 2.1 eV to 1.3 eV. We report in depth optical and X-ray spectroscopic study of Ruddlesden-Popper series of the perovskite sulfide, Baₙ₋₁ZrₙSnₙ₋₁S₂n₊₁(0≤n≤1). The polycrystalline samples were synthesized with an iodine catalyzed solid state reaction, and single crystals were grown with salt flux methods. Structural, chemical, and thermogravimetric studies establish that these materials have good optoelectronic properties and stability. High external luminescence efficiency, up to 0.15%, is obtained via quantitative photoluminescence measurements. An effective, bulk minority carrier lifetime longer than 65 ns and very low surface recombination are determined from time-resolved photoluminescence measurements. X-ray absorption spectroscopy illustrates the role of Zr-S covalent bonding in determining the electronic structure.

References:

8:30 AM ET05.10.03
From 3D to Lower Dimensional Perovskite Structures—The Change in Mobility and Solar Cell Performance Noor Titan Putri Hartono1, Shijing Sun1, Matthew Erodiţ2, Maria C. Gêlvez-Rueda3, Fengxia Wei4, Ferdinand C. Grozema5, Meng-Ju Sher2, Juan-Pablo Correa-Baena6 and Tonio Buonassisi2; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Wesleyan University, Middletown, Connecticut, United States; 3Delft University of Technology, Delft, Netherlands; 4Institute of Materials Research and Engineering, Agency for Science Technology and Research, Singapore, Singapore.
Although lead-halide perovskites (LHP) solar cells have reached 22.7% efficiency to date, they still face stability issues. Recent studies have suggested that shifting to lower dimensional (LD) perovskite structures may extend the cell’s environmental stability. However, these LD perovskite structures tend to have low photocurrents and solar cell performance. It has been suggested that their culprit is not only lifetime, but also their charge-carrier mobility. To understand this, we conducted a detailed study using PbI$_2$-based LD perovskites, which are synthesized by intentionally introducing a pre-defined amount of large A-site cations to force the structure to split into a layered compound. We measure the LD perovskite device performance, and characterize the absorber using THz spectroscopy and time-resolved microwave photocconductivity to understand the mobility. Finally, we relate the mobility results with the structures and device performances.

8:45 AM ET05.10.04
Role of Anion Vacancies in Light-Induced Halide Phase Segregation in MAPb(I$_{1-x}$Br$_x$)$_3$ Anthony Ruth, Michael C. Brennan, Sergiu Draguta, Yurii Morozov, Maksym Zhukovskyi, Boldizsár Janko, Peter Zapol and Masaru Kuno; 1University of Notre Dame, South Bend, Indiana, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.

Solution-processed mixed halide perovskites (e.g. MAPb(I$_x$Br$_{1-x}$)$_3$) are excellent materials for multi-junction solar cells due to their ideal characteristics, which include large optical absorption coefficients, long carrier diffusion lengths, long-lived carrier lifetimes, and tunable bandgaps. Unfortunately, light-induced halide phase segregation has prevented their effective integration into working devices. We present kinetic Monte Carlo simulations and complementary optical experiments which show that during illumination, halide migration is directed by the energetics of charge carriers. The nucleation of a low-bandgap, I-rich domain emerges as a mechanism to trap charge carriers and reduce their energy. Furthermore, migration rates in stoichiometric and halide-deficient MAPb(I$_x$Br$_{1-x}$)$_3$ thin films are dictated by halide vacancy hopping barriers and are modulated by the number of available vacancies. An established photosegregation excitation intensity threshold is independent of the number of vacancies and instead depends critically on parameters such as carrier diffusion length, lifetime and bandgap tunability. Superb agreement with experimental nucleation kinetics and optics validates the model and prompts its application to fundamental, experimentally-immutable aspects of photosegregation. By simulating nucleation with varying ionic mobilities, we determine how domain formation is influenced by species dependent I vs. Br diffusion rates and asymmetric hopping in tetragonal vs. cubic symmetry. The simulations further suggest that near ubiquitous emission energies, which converge on that for MAPb(I$_{1-x}$Br$_x$)$_3$ (i.e. x~0.2) following photosegregation, arise from the existence of kinetically trapped Br within nucleated I-rich domains surrounded by a pure I barrier. These simulations ultimately reveal that the ideal characteristics of mixed halide hybrid perovskites, specifically their large carrier diffusion lengths, are responsible for inducing photosegregation. The study thus sheds new light on important parameters that define photoinduced halide phase segregation in mixed halide hybrid perovskites and presents opportunities for ultimately controlling as well as employing the phenomenon.

9:00 AM ET05.10.05
Suppression of Halide Ion Exchange in Cesium Lead Halide Perovskites with PbSO$_4$-Oleate Capping Prashant Kamat, Vikashkumar Ravi and Rebecca A. Scheidt; University of Notre Dame, Notre Dame, Indiana, United States.

Metal halide perovskites are ionic in nature and their properties can be tuned through the exchange between halide ions. For example, by tailoring the ratio of Cl:Br and Br:I it is possible to modulate the absorption and emission properties of metal halide perovskites across the entire visible region. However, the ease of halide ion exchange poses a problem to create a tandem structure with layers of metal halide perovskites of different compositions. In order to keep the lead halide perovskite nanocrystals intact without undergoing exchange of halide ions and retain the original band structure one needs to suppress the halide ion migration across the nanocrystals. We have now successfully achieved this task by capping CsPbBr$_3$ and CsPbI$_3$ nanocrystals with PbSO$_4$-Oleate. The linear assembly of the nanocrystals that resemble that of a peapod structure inhibits the exchange of anions. Absorption measurements show that the nanocrystal assemblies maintain their identity as either CsPbBr$_3$ or CsPbI$_3$ for several days. Furthermore, we have electrochemically deposited these assemblies as hierarchical structures on electrode surfaces and employ them in light emitting devices. The effectiveness of PbSO$_4$-Oleate capping of lead halide perovskite nanocrystals offers new opportunities to overcome the challenges of halide ion exchange and aid towards the tandem design of perovskite light harvesting assemblies.

9:30 AM ET05.10.06
Titanium-Based Halide Perovskite Thin Films for Photovoltaic Applications Min Chen, Minggang Ju, Xiao Cheng Zeng, Yuanyuan Zhou and Nitin Padture; 1Brown University, Providence, Rhode Island, United States; 2Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

Lead-based halide perovskites have demonstrated superior optoelectronic properties since the emergence of perovskite solar cells (PSCs). However, the toxicity and phase stability of lead halide perovskites brings inevitable concerns with the practical application for the solar panel. Based on the environmental friendly element of Titanium (Ti), we have predicted a series of Ti vacancy-ordered double perovskite compounds, Cs$_2$Ti$_x$I$_{2-x}$, Rb$_2$Ti$_x$I$_{2-x}$, K$_2$Ti$_x$I$_{2-x}$ and In$_2$Ti$_x$I$_{2-x}$, which possess optimal bandgap and suitable absorption. Here, we successfully synthesis the Titanium-based materials which indicates the design of perovskite light harvesting assemblies. Thus, this work provides new direction in the design and development of high performance Ti-based thin-film PSCs of the future.

9:45 AM BREAK

10:15 AM ET05.10.07
Accessing Small Bandgaps in Halide Double Perovskites Adam H. Slavney, Linn Leppart, Abraham Saldivar Valdes, Davide Bartesaghi, Tom Savemije, Jeffrey B. Neaton and Hemamala Karunadasa; 1Stanford University, Stanford, California, United States; 2University of Bayreuth, Bayreuth, Germany; 3Delft University of Technology, Delft, Netherlands; 4University of California, Berkeley, Berkeley, California, United States.

The outstanding photophysical properties of APbX$_2$ perovskites (A = organic/inorganic monocation, X = halide) for optoelectronic applications has prompted a vigorous search for analogs. Indeed, finding structural and functional analogs is a time-tested approach for both better understanding the current champion material as well as for paving the way for second-generation materials. In this regard, there has been intense recent interest in the photophysical properties of halide double perovskites, where Pb$_2$ sites are replaced by two different metals that yield an average charge of 2+. However, despite this compositional versatility, all double perovskites with different metals have so far featured large bandgaps of ca. 2 eV or more. Although oxide perovskites feature both high-bandgap insulators and metals, such diversity has not yet been seen in their halide analogs. I will present work from our labs aimed at understanding how to manipulate the electronic structure of halide double perovskites through substitution chemistry. I will describe new design rules that have enabled the synthesis of halide double perovskites with unprecedented small (direct) bandgaps. We expect this work to aid in considerably expanding the electronic portfolio of halide perovskites for fundamental studies and applications in technology.
Lead-free perovskite solar cell is one of the research issues on perovskite solar cells. We have focused on Sn perovskite material. One of these Sn-related solar cells is SnPb mixed metal perovskite solar cell. We discuss how to enhance the efficiency from the view point of less trap densities in hetero-interfaces and the bulk layer. Sn2 Fambed perovskite layer and the introduction of spike band structure in the cell gave SnPb perovskite solar cells with 19% efficiency. The results lead us to developing Pb-free Sn-related perovskite solar cells. Pb of SnPb perovskite layer was replaced by Ge. We developed a new type of SnGe mixed metal perovskite solar cells and reported with enhanced efficiency and stability. XRD spectra showed that the structure is perovskite. The structure of GeSn perovskite was discussed from the view point of the band structure, XPS analysis, and the Urbach energy. Most of the Ge atoms are at the hetero-interface of the perovskite/PEDOT-PSS as well as at the interface of the perovskite/C60. They passivate the surface of the Sn perovksite (so-called graded structure). For SnGe(0)-PVK device, where SnGe(x) stands for SnGe perovskite with X% Ge content, the PCE was 3.31%. Upon doping with 5% Ge, the overall efficiency was enhanced to 4.48%. With the Ge content more than 10%, all the photovoltaic parameters decreased significantly which resulted in an efficiency as low as 0.80% for SnGe(0.2)-PVK device. After optimization, 7.89% of SnGe(5)-PVK device is reported. In addition, the stability of the device in air without encapsulation has been improved significantly with the Ge doping. 80% of efficiency was kept after doping with Ge (5%) from its original performance. However, only 10% of the efficiency was retained for nondoped sample SnGe(0). This work provides a platform for further research on lead-free SnGe-based perovskite solar cells.

Optoelectronics Studies Based on Two-Dimensional Hybrid Perovskite

Mauricio Solis de la Fuente, Sumanjee Kaur, Dalia Martinez Escobar, Selene M. Coria and Ravi Prasher; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Hybrid Perovskite solar cells have been the subject of intense interest due to significant optoelectronic properties (high absorbance, long diffusion length, etc.). An accelerated competition is taking place to obtain highest performance in single junction and tandem solar cells with efficiencies up to 20%. Nevertheless, huge scientific problem remains be solved that directly impact performance and future commercialization, namely the stability under external agents as light, oxygen, humidity and heat. The organic ions play an important role in the perovskite stability, which make them sensitive to moisture; Some studies showed the perovskite 2D are more resistant to humidity conditions in contrast to 3D. However, a decrement in density of carriers photogenerated is obtained where the vertical orientation is wishing to get good performance in solar cells. We explore other strategies to extract carriers mainly doping 2D perovskite with single walled carbon nanotubes and graphene. Experimental measurements to explain how structural changes (domain distributions, band gap positions) can modify optoelectronics properties as photoluminescence, conductivity, Seebeck coefficient, I-V curves and absorbance will be discuss.

References

Edge Management in Reduced-Dimensional Perovskites Enables Efficient and Stable Light-Emission

Lina Qian1, 2 and Edward H. Sargent1; 1University of Toronto, Toronto, Ontario, Canada; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Halide perovskites, especially layered quasi-2D perovskites, offer a number of advantages to creating bright and efficient light-emitting applications. Their combination of excellent charge carrier mobility and low density of recombination centers have enabled their rapid ascent in electroluminescent devices. Halide perovskites, especially layered quasi-2D perovskites, offer a number of advantages to creating bright and efficient light-emitting applications. Their combination of excellent charge carrier mobility and low density of recombination centers have enabled their rapid ascent in electroluminescent devices. To bring perovskite LEDs to commercialization, a remaining issue of stability needs to be addressed. In this presentation, we pinpointed the chief cause of the dramatic degradation of halide perovskites in light-emitting diodes (LEDs). We studied photogenerated charges accumulating at exposed perovskite facets activate the physisorbed oxygen, converting it into reactive superoxide that triggers perovskite degradation. We thus aimed at developing a strategy to protect the perovskite facets. At an applied level, we achieve perovskite films that exhibit a near-perfect passivation, attested to by their photoluminescence quantum yields (PLQY’s) that closely approach 100%. These films are stable under continuous illumination in ambient conditions over hundred hours. In addition, we report orders of magnitude improvement in device operating stability relative to the best-performing prior perovskite reports.

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References
Metal halide perovskites are generating enormous interest for their use in optoelectronic devices including photovoltaics and light-emitting diodes. One of their most remarkable properties is their apparent defect tolerance – films can be produced using relatively crude processing methods yet they still exhibit very good device performance. Calculations have suggested that this is at least partly because many defects cause only shallow trap states which may not be catastrophic for device performance (unlike deeper trap states). Nevertheless, there is still substantial non-radiative losses suggesting defects are not entirely benign and they still must be understood and addressed before devices can approach their performance limits.

Here, I will cover our ongoing work focusing on defects and their impact on non-radiative losses, as well as their mitigation through passivation treatments. I will present recent results in which we use multimodal approaches to determine relationships between local chemistry, structural and luminescence properties in perovskite thin films using synchrotron nano X-Ray Diffraction (n-XRD) and nano X-Ray fluorescence (n-XRF) measurements, as well as confocal and wide-field luminescence imaging. We reveal an intimate connection between strain and non-radiative decay, revealing these strain-related defects as a primary origin of non-radiative losses. I will also outline the action of passivation treatments, such as chemical and light-induced treatments, on relieving these strain patterns.

The work provides a platform for designing new and more effective passivation post-treatments or film fabrication methods, which will push devices ever closer to their efficiency limits.
properties, and chemical segregation. We reveal that the methylammonium segregation leads to a decrease of electronic conductivity and an increase of ionic conductivity. Overall, this work provides new insights into understanding the role of the twin domain in photovoltaic action.

2:45 PM ET05.11.04
Phase Intergrowth and Structural Defects in Organic Metal Halide Ruddlesden–Popper Thin Films Naveen Venkatesan1, Rhiannon Kennard1, Ryan A. DeCrescent1; Erin Perry1, Clayton J. Dahlman1, David Hanifi2, Jon A. Schuller1, Alberto Salleo1 and Michael L. Chabinyc1; 1University of California, Santa Barbara, Santa Barbara, California, United States; 2Stanford University, Stanford, California, United States.

Hybrid organic metal halide Ruddlesden-Popper (R-P) phases have recently been the subject of intense research efforts due to their good power conversion efficiencies in photovoltaics and controllable emission for light emitting diodes, while possessing better environmental stability compared to their three-dimensional counterparts. The thin film structures of these layered perovskites are still poorly understood relative to the bulk. In this study, we use optical spectroscopy, X-ray scattering, and transmission electron microscopy to characterize the structures of these thin films of (CH$_3$NH$_3$)$_2$(CH$_3$NH$_3$)$_2$PbI$_4$ and (CH$_3$NH$_3$)$_2$(CH$_3$NH$_3$)$_2$PbI$_6$ on the meso- and nanoscale. Previous studies suggest a preferential orientation of the Pb-I sheets in spin coated films perpendicular to the substrate, so that the layer stacking direction is in the plane of the film. By measuring in-plane and off-specular X-ray diffraction with grazing incidence wide-angle X-ray scattering (GIWAXS), we observe that some expected peaks along the stacking direction of the Pb-I sheets are missing, indicating disorder in perovskite layer stacking. Because the diffraction patterns represent a bulk, average structure, we used transmission electron microscopy (TEM) to explore film structure on a local scale and find that these films consist of small crystalline grains in an amorphous matrix, contradictory to previous reports suggesting single-crystalline quality thin films. When using known crystal structures to index these SAED patterns, we see that the thin films comprise not only the targeted R-P phase, but also regions with lower and higher Pb-I sheet thickness (i.e. phase impurities). This phase intergrowth creates structural defects that interrupt layer stacking and is the cause of broadening of in-plane diffraction peaks, causing them to be absent from previous GIWAXS measurements. Finally, because these films produce efficient photovoltaics despite this high degree of structure disorder, we measured the absorption coefficient using photothermal deflection spectroscopy (PDS) and find Urbach energies of 32 meV for the R-P phases compared to 19 meV for methylammonium lead iodide. Despite the structural defects, the R-P films appear to maintain a low degree of electronic disorder suggesting that the Pb-I regions are electronically isolated from each other.

3:00 PM ET BREAK

3:30 PM ET05.11.05
Hybrid Inorganic-Organic Perovskites—From Film Optical Response to Device Functionality Nikolas Podraska, Biwas Subedi, Kiran Ghimire, Prakash Upety, Maxwell Junda, Cong Chen, Chongwen Li, Dewei Zhao, Zhaoning Song and Yanfa Yan; University of Toledo, Toledo, Ohio, United States.

Solar cells with hybrid inorganic-organic lead halide based perovskite absorber layers have achieved remarkably high photovoltaic device performances in a relatively short amount of time when compared to comparable devices based upon other semiconductor absorbers. This perovskite family offers a wide range of tunable opto-electronic properties obtained via alloying of either / both the organic and inorganic components, and, even in their polycrystalline form, these perovskites are generally quite electronically forgiving semiconductors. However, as the material composition is manipulated, film stability and any increase in defect concentration remain issues. Here we will provide an overview of the optical properties, in the form of the complex index of refraction or complex dielectric function spectra, as well as the physical origin for the features present in those optical properties for perovskite layers with considerations toward composition, sample handling / environmental exposure, and incorporation in devices. Proper measurement and analysis yielding accurate values of the complex optical properties over the ultraviolet to millimeter wavelength range and complementary techniques sensitive to different levels of optical absorption enables tracking of the bandgap and higher energy critical point transitions, electrical transport properties manifested as free carrier absorption, sub-bandgap absorption due to defects, and film degradation or decomposition upon atmospheric exposure as deduced from in-situ / ex-situ spectroscopic ellipsometry, optical Hall effect, and photothermal deflection spectroscopy. Once acquired, these optical properties serve as input for external quantum efficiency simulations of photovoltaic device performance. Features observed optically will be correlated with full functioning device performance, illustrating how accurate optical property measurements over different wavelength ranges and levels of absorption provide insight into device functionality.

4:00 PM ET05.11.06
In Situ TEM Observation of Perovskite Solar Cells Satoshi Uchida1, Tae Woong Kim1, Ludmila Cojocaru2, Takashi Kondo1 and Hiroshi Segawa1; 1The University of Tokyo, Tokyo, Japan; 2University of Freiburg, Freiburg, Germany.

Recently, organometal halide perovskite solar cells (PSCs) have received great attention. The power conversion efficiency (PCE) of PSCs have shown a dramatic increase and certified PCEs adopting mixed organic cations and halide anions have reached over 22%. The PCE is considerably affected by photovoltaic property of each component of a PSC. In spite of the significance in the crystallographic information, however, microstructural observation for crystal structure analysis of the perovskite layer has not been actively conducted. Until now it is widely believed that each phase of the organometal halide perovskite solely exists with orthorhombic phase < 165K < tetragonal phase < 327K < cubic phase. Nevertheless we newly observed that the tetragonal and cubic phases coexist at room temperature in the conventional MAPbI$_3$ thin film device. Furthermore, surprisingly, superlattices composed of mixture of tetragonal and cubic planes without any compositional change was also found. Formation of the superlattice is achieved by only intrinsic structural transition without artificial modifications and, therefore, most phenomena concerned with the superlattice are expected to spontaneously and automatically occur in context with situation. The organometal halide perovskite self-adjusts their microstructural configuration and self-organizes buffer layers inside crystal or at hetero-interface by introducing the self-assembled superlattices. We believe, this report will be a vital cornerstone to bring the PCEs of the organometal halide perovskite solar cells one step closer to theoretical maximum point and redefine possibility of the organometal halide perovskite as promising materials for not only solar cell but also various application.

4:15 PM ET05.11.07
Strain Effect on Stability and Band Gap in CsPbBr$_3$ Crystal via NanoXRD Xueying Li1, Yaniqi Luo1, Moses Kodur1, Rishi Kumar1, Martin V. Holt2, Zhonghou Cai2 and David P. Fenning1; 1University of California, San Diego, La Jolla, California, United States; 2Argonne National Laboratory, Argonne, Illinois, United States.

Despite the comparable power conversion efficiency between polycrystalline Si and perovskite solar cells (PSC), the commercialization of PSCs is inhibited by their low stability. A recent study demonstrated that the commonly used spin-casting and annealing for perovskite thin film create strain in the material and lead to decreased stability. Other publications have observed an association between lattice constant and band gap in halide perovskites ABX$_3$ (A= methylammonium, formamidinium, cesium; B=lead; X=Bromide, iodide, chloride), suggesting their band gap can be tuned through the manipulation of strain in the material. However, the knowledge of strain distribution and its local effect is lacking for making highly stable PSCs or stress...
sensitive optoelectronics. To study the local effect of strain, we map CsPbBr$_3$ crystals with nanoscale X-ray Diffraction Microscopy (nanoXRD) with approximately 100-nm spatial resolution and 0.1% sensitivity in strain detection. By exploiting the thermal expansion coefficient mismatches, a strain gradient is created in a CsPbBr$_3$ crystal at the edge of a platinum pad on quartz substrate and characterized by nanoXRD. We find that the observed compressive strain reduces the stability of the material, which proves that strain should be avoided for highly stable halide perovskites. We also characterize the same crystal with ex-situ photoluminescence (PL) mapping and observe PL peak shifts red at compressively strained locations in the crystal. This demonstrates the band gap narrowing by substrate-induced strain locally, which should be brought into attention for the fabrication process of halide perovskites on substrates. On the other hand, the strain effect on band gap shows potential of stress-sensitive optoelectronic applications with halide perovskites.

4:30 PM ET05.11.08
Probing the Microstructure of Methylammonium Lead Iodide Perovskite Solar Cells Tobias Leonhard, Holger Röhm, Alexander Schulz, Fabian J. Altermann, Susanne Wagner, Wolfgang Rheinheimer, Michael J. Hoffmann and Alexander Colsmann; Karlsruhe Institute of Technology, Karlsruhe, Germany.

The microstructure of absorber layers is pivotally important for all thin-film solar technologies. Despite its unprecedented performance development in recent years, little is known about the microstructure of metal-halide perovskites and its effect on the macroscopic device performance. Yet, recent publications have frequently called attention to the urgent need of spatially resolved microstructure characterization techniques in order to correlate the microscopic structure with macroscopic device properties.

In this work, we report on the spatial investigation of methylammonium lead iodide (MAPbI$_3$) grain properties by electron backscattered diffraction (EBSD) with high resolution. We resolve diffraction pattern ambiguities that are related to the close-to-cubic perovskite unit cell, and develop a comprehensive three-dimensional picture of the crystal orientation. We identify predominant orientation directions and observe orientation cross-talk between neighboring grains. The local crystal information correlates with ferroelectric and electronic properties that we probe with piezo-response force microscopy (PFM) and kelvin probe force microscopy (KPFM) measurements. If the ferroelectric polarization influences the charge carrier recombination and transport, as was predicted by simulations, then the orientation and shape of polarized domains within grains would directly influence the device performance. In turn, this renders engineering of the grain orientation and size a pivotal parameter for the optimization of perovskite solar cells, which is not yet commonly investigated in most perovskite solar cell studies. These tools are indispensable for the future relation of the microscopic structure to the optoelectronic properties of perovskite devices as they allow to monitor device optimization and to understand fundamental processes of perovskite solar cells. Therefore, we expect EBSD and PFM to become the most often employed characterization techniques in the future for the correlation of microscopic structure and macroscopic device performance. Their strong correlation allows to draw conclusions about the microstructure from ferroelectric features and, likewise, to derive the ferroelectric polarization from crystallographic observations. Understanding the microstructure would not least be the key to future ab-initio engineering of new (non-toxic) and highly efficient perovskite solar cells.

References

4:45 PM ET05.11.09
Direct Optical Identification of Grain Boundaries and Carrier Diffusion in Perovskite Film Wenhao Li, Srinivas K. Yadavalli, Yuanyuan Zhou, Nitin P. Patude and Rashid Zia; Brown University, Providence, Rhode Island, United States.

Perovskite solar cells (PSCs) have attracted considerable attention in recent years due to their rapidly increasing power conversion efficiency (PCE), which currently exceeds 22%. Given that most high efficiency PSCs are made of polycrystalline films, an important feature is their grain size distribution, because grain boundaries can limit carrier diffusion and serve as nonradiative recombination sites, thereby reducing the PCE. Due to the formation of grain boundary grooves during perovskite film growth, many techniques for estimating grain size rely on surface morphology characterization using scanning electron microscopy (SEM) or atomic force microscopy (AFM). However, not all grain boundaries exhibit clear topographical features.

Here, we report the direct identification through photoluminescence (PL) microscopy of grain boundaries in formamidinium lead iodide (FAPbI$_3$) thin film samples that cannot be observed by either SEM or AFM. We demonstrate that these "invisible" boundaries impede carrier diffusion and limit radiative recombinations events. Optical characterization is further supported by electron backscatter diffraction (EBSD) measurements that are used to confirm crystal orientation differences across these otherwise imperceptible boundaries. Then, we present PL lifetime measurements that show how these "invisible" boundaries serve as nonradiative recombination sites, thereby decreasing carrier lifetimes, and likely reducing PCEs.

In order to quantify the carrier diffusion resistance in different types of grain boundaries, we developed a carrier density probing method. Using a high-speed intensified emCCD camera, we are able to measure the 2D PL intensity distribution with nanosecond resolution. Comparing the PL distribution with excitation near and far away from the grain boundary, we can see the effect of grain boundaries in blocking carriers. A carrier diffusion and recombination model is used to fit the observed PL evolution to extract the diffusion and recombination coefficients. Together with a mapping of steady state PL intensity distribution and the carrier density probing method, we are able to estimate the resistivity of carrier diffusion across grain boundaries.

Finally we will discuss the impact of these boundaries as well as this new characterization method for the synthesis and analysis of thin-film perovskite solar cells.

SESSION ET05.12: Poster Session IV: Fundamentals of Halide Perovskite Optoelectronics
Session Chair: Ivan Mora-Sero
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET05.12.01
Impact of Applied Bias, and Material Degradation on Ion Transport in Hybrid Perovskite Solar Cells Under Illumination Emily C. Smith1, Christie Ellis1, Hamza Javaid1, Lawrence A. Renna1, Yao Liu1, Thomas P. Russell1,2, Monojit Bag1 and Dhandapani Venkataraman1; 1University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.
We mapped ion transport in hybrid organic–inorganic perovskite solar cells under illumination using impedance spectroscopy (IS) as a function of applied bias and device degradation. We observe evidence of mass (ion) diffusion and extraparticle conductivities (∼10^-7 S cm^-1) for the mobile ionic species at varying applied biases. We show that ions respond to low applied forward bias in a predictable manner, characterized by an increased double layer capacitance at the hole-transporting (HTM) and electron-transporting material (ETM) interfaces. This is presumably due to ion accumulation and electrical charge pinning or screening effects under external biasing. Unexpectedly, at high forward biases, we found that there is a capacitative discharge in the double layer resulting in ion redistribution in the bulk. Furthermore, we show that double-layer capacitance as a result of ion accumulation significantly impacts the electronic properties of the device and thus device performance. Lastly, we show that as the device degrades there is an overall depletion of capacitative effects coupled with increased ion mobility.

**ET05.12.02 Understanding the Solvent Engineering Method Through In Situ Time-Resolved GIWAXS**

**Rodrigo Szostak**, Paulo E. Marchezi, Adriano Marques, Marco S. Medeiros, Jeann C. Silva, Matheus Holanda, Hélio N. Tolentino and Ana F. Nogueira; University of Campinas, Campinas, Brazil; Brazilian Synchrotron Light Laboratory, Campinas, Brazil.

Organic inorganic hybrid perovskites (OHP) is the most promising material to achieved photovoltaic devices with high power conversion efficiency and low cost. The perovskites with the composition Cs$_x$FA$_{1-x}$PbBr$_3$ achieve high PCE, present better stability, photostability, and their band gap can be tuned by changing the composition, becoming interesting for tandem solar cells. The most used method to prepare this sort of composition is the solvent engineering method [1]. During the spin coating process, an antisolvent (chlorobenzene, dichlorobenzene, toluene) is dropped onto the substrate to remove the excess of the original solvents as DMF and DMSO. Thus, formation of perovskite or an intermediate can be attained. Despite of being the most popular method, the impact of many deposition parameters such the time to inject the anti-solvent, the molar proportion between the precursors and DMSO during the spin coating, are not well understood. Here we used in situ time-resolved grazing incidence wide-angle X-ray scattering (GIWAXS) in the Brazilian Synchrotron Light Laboratory (LNLS) during film preparation to monitor and get insights about the perovskite formation. Cs$_{1.5}$FA$_{0.5}$Pb(Br$_{0.87}$I$_{0.13}$)$_3$ was the composition of choice. Without antisolvent, the main scattering signal is attributed to a disordered colloidal gel formed between perovskite and solvent. [2] This signal fades with time, and the lifetime changes with DMSO perovskite proportion and ambient moisture. Immediately after anti-solvent injection, new XR D peaks emerged attributed to α-phase of the perovskite and intermediates. The intermediates’ peaks fade with time while the peak related to the perovskite becomes more intense. The results reveal that perovskite formation takes place without thermal annealing and the transformation occurs through the intermediates. With shorter times of anti-solvent injection, the morphology of the film is smooth, but with longer times, the morphology becomes more heterogeneous. This was attributed to intermediates formed before the injection of the anti-solvent, that remain stable in the film. In conclusion, in situ time-resolved GIWAXS during the spin coating step provided important information about the best parameters to guarantee only perovskite formation or intermediates with shorter “lifetime”. Having these parameters in hands, films with better morphology, transport and optoelectronic properties can be obtained.

**ET05.12.03 Exceptional Grain Growth in Formamidinium Lead Iodide Perovskite Thin Films Induced by Phase Transformation**

Srinivas K. Yadavalli, Yi Zhang, Wenhao Li, Yuanjuan Zhou, Rashid Zia and Nitin P. Padture; Brown University, Providence, Rhode Island, United States.

Formamidinium lead iodide (FAPbI$_3$) based perovskites have attracted a great deal of interest as light absorbers in solar cells due to their superior thermal stability and more suitable band gap compared to perovskites based on methylammonium (MA). However, preferential formation of a photo-inactive α-FAPbI$_3$ phase at room temperature has been a major impediment. The need for prolonged heat-treatments at temperatures >150 °C to obtain the desirable α-FAPbI$_3$, perovskite phase often leads to film degradation. Heat treatment also produces fine-grained films with high grain-boundary density, which is detrimental to PSCs performance and stability. In this context, we have discovered a new phenomenon, where fine-grained (∼175 nm) α-FAPbI$_3$, thin films transform rapidly to phase-pure α-FAPbI$_3$, perovskite thin films with ultra-large grain size exceeding ∼5 μm. The large-grained nature of the film is confirmed using appropriate materials characterization techniques. The improved kinetics of transformation is explained by studying the phase and morphological evolutions during film-solvent interaction. The nature of phase nucleation and growth is studied through in-situ microscopy techniques. In situ X-ray diffraction and solvent polarity effects on the transformation rate are also studied to corroborate the proposed mechanism. Devices with high efficiency are fabricated with these ultra-large grained films and are characterized. The use of this novel approach to achieve 5-μm grains by a brief low-temperature treatment enables a promising path toward achieving ‘single-crystal’ films with superior optoelectronic properties and chemical stability.

**ET05.12.04 Surface Doping of Metal Halide Perovskites**

Nakita K. Noel, Alba Pellaroque, Federico Pulvirenti, Henry Snaith, Seth R. Marder and Barry P. Rand; Princeton University, Princeton, New Jersey, United States; Physics, University of Oxford, Oxford, United Kingdom; Chemistry, Georgia Institute of Technology, Atlanta, Georgia, United States.

Within the past few years, metal halide perovskites have been attracting significant interest due to their successful application to optoelectronic devices. These materials have been used in lasers, photodetectors, and most commonly, in photovoltaic devices and light emitting diodes. Despite the cheap and simple fabrication methods by which these materials are deposited, high quality perovskite films can be readily fabricated, and the power conversion efficiencies of lead halide perovskite solar cells are now approaching certified values of 23%. However, perovskite-based devices are yet to achieve their full potential. One of the major hindrances to achieving this potential is an incomplete understanding of perovskite surfaces and interfaces. Deficiencies at these interfaces may be responsible for the largest losses in perovskite based optoelectronic devices; hindering charge extraction, increasing non-radiative recombination rates and hysteresis, and significantly increasing the voltage loss in perovskite photovoltaics. We propose surface doping the perovskite material as a means to combat these interface deficiencies. Herein, we will discuss doping of the perovskite material at various interfaces using well-established charge-transfer dopants. We show the doping of the perovskite material through both solid-state NMR and surface characterisation techniques, and further characterise the material through photoluminescence measurements, showing a reduction in the non-radiative recombination of the material. Using this surface doped material, we show photovoltaic devices with reduced hysteresis, low voltage losses, and steady-state power conversion efficiencies in excess of 20%.

**ET05.12.05 Advances in Bright Single Layer Perovskite Light Emitting Devices**

Ross E. Haroldson, Artur Išlštev, Patricia Martinez, Mosad Alahbadkhi and Anvar A. Zakhidov; The University of Texas at Dallas, Richardson, Texas, United States; MISIS, Moscow, Russian Federation.

Exciting reports about single layer cesium lead iodide perovskite LEDs have shown that conventional electron and hole injection layers are not necessarily needed. A sandwiched device structure consisting of a perovskite-polymer composite film between two electrodes can emit bright light at low operating and threshold voltages (∼2–20 volts). We studied the role of grain size, polymers inclusion, morphology, emission changes, and electrode material in CsPbBr$_3$ based LED. These simple single layer devices are easier and cheaper to fabricate as compared to their multilayered counterparts and removes the possible reaction routes between perovskite and the charge injection layers. We also investigate underlying mechanisms of how ion migration within the
perovskite layer forms a p-i-n junction which allows efficient charge injection directly from the electrodes, independently of their work function, while still having efficient radiative recombination.

**ET05.12.06**  
*Photo-Stable Bismuth Doped MAPbI₃ Thin Films for Optoelectronics Devices*  
Carlos D Redondo-Obispo¹, Teresa S Riplolles¹, Esteban Ciment-Pascual¹, Javier Bartolomé-Villchez², Alicia de Andrés³ and Carmen Coya¹; ¹ETSIIT, Universidad Rey Juan Carlos, Madrid, Spain; ²ETSI Industrialies, Universidad Politécnica de Madrid (UPM), Madrid, Spain; ³Facultad de CC. Fisicas, Universidad Complutense de Madrid (UCM), Madrid, Spain; ⁴Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Madrid, Spain.

Hybrid organic-inorganic perovskite research continues gaining efforts to achieve high overall photoconversion efficiencies due to their unique optoelectronic properties. [1] An intense activity is dedicated to overcome their high sensitivity to ambient atmosphere (especially water and oxygen) and to visible irradiation that strongly handicap their stability and performance. In particular, semiconductors doping strategy with heterovalent ions has been tested to stabilize the perovskite material, to control phase transition, morphology improvements, or enhance the electrical and optical properties. Obtaining more stable compounds as well as understanding the complex behavior of the emission evolution upon illumination and time are main concerns to be addressed. The photoluminescence behavior is strongly sensitive to different parameters, mainly to the presence of defects and traps whose evolution with time is related to ion migration and perovskite transformations. [2, 3]

In the present work, the incorporation of Bi₃⁺ in the MAPbI₃ (MA=CH₃-NH₂) perovskite precursor solution leads up to around 7 at.% incorporation at the time is related to ion migration and perovskite transformations. [2, 3] ca. 15% while the usual spurious PbI₂ phase in undoped films is not observed for any Bi doping. Influence on optical and electrical properties are also studied. Novel effects as extraordinary photostability and photosensivity enhancement, compared to that of undoped MAPbI₃ thin films are observed.

Bi³⁺ incorporation lead to a slight increment of the optical gap due to the reduction of lattice parameters. However, for the photoluminescence properties, the phenomenology for the Bi³⁺ doped samples is drastically different at high power irradiation. We propose a mechanism to explain the observed trends using a model based on the migration of Bi³⁺ upon irradiation and its effect on the MAPbI₃ cell volume and bandgap energy. These results provide a new path for obtaining highly stable materials which would allow an additional boost of hybrid perovskite based optoelectronics.


**ET05.12.07**  
*Nanoimprinted Plasmon Enhanced Perovskite Solar Cells*  
Tianyi Shen, Stylianos Siontas and Domenico Pacifici; School Engineering, Brown University, Providence, Rhode Island, United States.

Perovskite solar cells have drawn great attention in the past years. Besides the high absorption and long carrier diffusion length of the material, perovskite solar cells have demonstrated potential for a promising alternative to conventional silicon solar cells due to their lower fabrication costs and reported power conversion efficiencies reaching 22.1%.

Plasmonic absorption enhancement has been extensively utilized to improve the performance of various solar cell technologies. Here, we report on a simulation study to further boost the efficiency of perovskite solar cells by embedding plasmonic concentrators in the back metal contacts. Specifically, three dimensional finite-difference time-domain (FDTD) simulations are performed on perovskite solar cells, consisting of perovskite films with varying thickness on top of flat or corrugated gold electrodes with varying light trapping geometries (nanodisk or nanohole arrays). The calculated electric fields in the simulation volume enable the decoupling of the absorption within the perovskite and gold films, respectively, which allows for the calculation of the cell power conversion efficiency (PCE) as a function of relevant design parameters. By systematically leveraging the geometry dimensions, the optimal nanostucture designs are obtained. The results show that 100nm-thick perovskite films on top of corrugated gold electrodes can exhibit up to 52% PCE increase compared to their flat counterparts (from 19.2% for a flat cell to 29.2% for an optimized nano-corrugated cell). Moreover, we show that a 150nm-thick perovskite film cell with opportunely corrugated back metal contacts can exhibit a PCE value (31.3%) comparable to that of a 400nm-thick bulk-like cell (31.6%).

These findings may pave the way for plasmon-enhanced high-performance thin-film perovskite solar cells fabricated via scalable methods such as nanoimprint lithography.

**ET05.12.08**  
*Long Electron–Hole Diffusion Length in High-Quality Lead-Free Double Perovskite Films*  
Weihua Ning, Feng Wang and Feng Gao; Department of Physics, Chemistry, and Biology (IFM), Linköping University, Linköping, Sweden.

Developing environmentally friendly perovskites has become important in solving the toxicity issue of lead-based perovskite solar cells. Here, the first double perovskite (Cs₅AgBiBr₆) solar cells using the planar structure are demonstrated. The prepared Cs₅AgBiBr₆ films are composed of high-quality double perovskite layers with diameters equal to the film thickness, thus minimizing the grain boundary length and the carrier recombination. These high-quality double perovskite films show long electron–hole diffusion lengths greater than 100 nm, enabling the fabrication of planar structure double perovskite solar cells. The resulting solar cells based on planar TiO₂ exhibit an average power conversion efficiency over 1%. This work represents an important step forward toward the realization of environmentally friendly solar cells and also has important implications for the applications of double perovskites in other optoelectronic devices.

**ET05.12.09**  
*Combinatorial Investigation of Coevaporated CsPbl₃ Thin Films with Large Quasi–Fermi Level Splitting*  
Pascal Becker¹, Pascal Becker², Jose Marquez Prieto³, Amran Al-Ashouri¹, Carlos Hages¹, Hannes Hempel¹, Justus Just¹, Steve Albrecht¹ and Thomas Unold¹; ¹Dept. Structure and Dynamics of Energy Materials, HZB, Berlin, Germany; ²Bergische Universität Wuppertal, Wuppertal, Germany; ³Lund University, Lund, Sweden; ⁴Young Investigator Group Perovskite Tandem Solar Cells, HZB, Berlin, Germany.
The new generation of photovoltaic materials is driven by the unprecedented rapid performance improvement of hybrid organic-inorganic perovskite solar cells (PSCs). Fully inorganic CsPbI3 perovskites have also demonstrated their great potential for photovoltaics in world record quantum dot solar cells as an ideal material candidate for tandem devices with a band gap close to 1.8 eV. In this study we explore the composition-dependent phase stability of CsPbI3 films by combinatorial studies. We show that coevaporated CsPbI3 can be synthesised in a stable perovskite phase under Cs rich conditions without the need of a post deposition annealing treatment. We investigate the compositional dependence of the electronic properties by THz spectroscopy and quantitative hyperspectral photoluminescence imaging. Compositional regions with considerably large carrier mobilities and a high photoluminescence quantum yield are identified. From these measurements a maximum quasi-Fermi level splitting of 1.27 eV and charge carrier diffusion lengths of around 3 microns are estimated, indicating this material’s potential for high efficiency solar cells. We find that the charge carrier mobility decreases with increasing Cs content corresponding to a lowering of the electronic dimensionality as the Cs content is increased in the films. First planar pin-type solar cells have been fabricated showing stabilised efficiencies exceeding 11%. Based on the comparison of the optoelectronic characterisation performed in the CsPbI3 films and the solar cells properties of the corresponding devices we conclude that the devices are strongly limited by interface recombination. Optimisation of the device architecture with better matched extraction layers exhibiting less interface recombination could be expected to lead to 18% efficient inorganic perovskite solar cells.

ET05.12.10
Photodetectors and Solar Cells Using Indium (I) Iodide as Active Material
Marina Ustimeny¹, Filipp Talalaev², Sergey Babenko¹, Sergey Luchkin¹ and Pavel Troshin¹; ¹Skolkovo Institute of Science and Technology, Moscow, Russian Federation; ²Institute for Problems of Chemical Physics of RAS, Chernogolovka, Russian Federation; ³The Branch of Talrose Institute for Energy Problems of Chemical Physics of Russian Academy of Sciences, Chernogolovka, Russian Federation.

Design of novel advanced semiconductor materials usually defines the progress in the development of new photovoltaic (PV) technologies. In particular, recently discovered lead halide based perovskites demonstrated outstanding electronic characteristics and showed high efficiencies of ~22% in single junction photovoltaic cells fabricated using low-cost solution process. Perovskite solar cells can potentially accomplish a revolution on the PV market due to their high efficiency and low cost. However, the practical application of perovskite photovoltaics is still limited severely by low stability of complex lead halides and their high toxicity. Therefore, many research groups worldwide explore different families of binary and complex metal halides with high electron/hole mobilities and long carrier lifetimes in order to find some feasible environment-friendly alternatives to the conventional lead perovskites. Boumassi et al. have presented recently theoretical and spectroscopic study suggesting that InI might be considered as a valuable material for photovoltaics (Chem. Mater. 2017, 29, 4667-74).

Here we present the first to the best of our knowledge experimental study of InI as semiconductor material for photovoltaic devices. Planar junction PV cells with InI as active material demonstrated encouraging external quantum efficiency of 17% at short wavelength, while the overall power conversion efficiency (~%1) was mainly limited by low open circuit voltages and fill factors even after substantial optimization of interfacial layers, active layer thickness and morphology. Strong photocurrent effect revealed for thin films of InI allowed us to apply this material for fabrication of efficient photodetectors with lateral and vertical geometries. Both types of devices showed excellent light sensitivity and short response times pointing towards high potential of further development of this research direction.

ET05.12.11
Energetics and Structural Effects of Degradation in Halide Perovskites
Colin Freeman, Christopher M. Handley, Derek Sinclair, Ian M. Reaney, Vikas Kumar and Cornelia Rodenberg; University of Sheffield, Sheffield, United Kingdom.

With the massive interest in halide perovskites there has been a wide range of research into combinations of these materials. MAPbI3, however, still demonstrates very desirable properties. The long term stability of MAPbI3 remains a significant challenge to any true commercial uptake. The degradation can be significantly affected by many factors but remains unclear [16]. Particular attention has focussed on the effect of non-stoichiometry of the material [19] which may have a significant role in the stability.

Simulations can provide a very valuable tool for studying the defect behaviour, stability and degradation of these perovskite materials due to their ability to design and explore exact conditions and examine the local atomic behaviour. Although very powerful, ab initio simulations are limited to modelling relatively small cells due to their computational demands. Classical mechanics provides a powerful method to reach larger sizes and far more configurations.

We use our recently published forcefield [3] to study defects in the MAPbI3 system. We observe that defects are encouraged by non-stoichiometry in the system. We examine the local and long range structural effects of the defects with a particular focus on dynamic behaviour in the ions (rotation/vibrations) and tilt of the octahedra. From this we are able to comment on the influence in general on degradation. We couple these results to experimental probing of degradation in non-stoichiometric samples.

[3] C.M. Handley, C.L. Freeman, PCCP 2017, 19, 2322

ET05.12.12
Understanding and Tuning the Energetic Landscape in Mixed Dimensionality Perovskites
Haralds Abolins and Felix Deschler; University of Cambridge, Cambridge, United Kingdom.

Ruddlesden-Popper perovskites have recently been shown possess greatly enhanced environmental and thermodynamic stability relative to their bulk counterparts, which has proven the key challenge for the commercialization of perovskite-based photovoltaics. Nevertheless, when these low-dimensionality materials are deposited in thin films through a fast crystallization process, a mixed phase material will result with bulk-like perovskite domains intermixed with grains of Ruddlesden-Popper perovskite of varying configurations in the number of atomic layers between each set of spacer cations. The precise composition will depend on processing conditions and will inevitably have an effect on the charge transport characteristics of the resulting material. While it has been shown that high-efficiency solar cells and LEDs can be fabricated from mixed dimensionality perovskites, the charge transport characteristics between the different phases in these materials have not been well understood. To elucidate the carrier dynamics in Ruddlesden-Popper perovskites a deposition procedure for obtaining thin films with micron-sized single-phase grains is developed. The spatial configuration of the various dimensionality phases is subsequently revealed through photoluminescence mapping and is shown to be tunable in both distribution and relative abundance by varying the deposition conditions. Lastly, it is demonstrated through spectrally resolved photoluminescence lifetime studies that charges are funnelled to the lowest band-gap phases of the materials through an energy transfer process that considerably increases local carrier concentration, leading
to enhanced photoluminescence quantum efficiencies. Crucially, the geometry, rate and efficiency of this funnelling are shown to be tunable through only slight adjustments in processing conditions, allowing the energetic landscape to be tailored for individual applications.

**ET05.12.13**

**Surface Ligands on Methylammonium Lead Iodide Perovskites—Binding Group Effects on Photoluminescence and Photovoltaic Device Performance**

So Min Park, Masud Abdullah A, Christopher I Richards and Kenneth R. Graham; University of Kentucky, Lexington, Kentucky, United States.

Organometal halide perovskites are emerging as promising photovoltaic (PV) materials due to their strong absorbance throughout the visible region, relatively high charge-carrier mobilities, and power conversion efficiencies (PCE) that are on par with polycrystalline silicon. As these materials progress towards commercial applications, understanding the factors limiting the PCE and stability is becoming essential. Interfaces and grain boundaries are some of the most influential aspects for both device performance and stability, as these are prime areas for defect formation and charge recombination. One means of improving both device performance and stability is to passivate these surfaces and grain boundaries by applying surface ligands. Although multiple surface treatments and additives have been applied to perovskite PVs, there is a lack of understanding of how these molecules are interacting with the perovskites. In this study, we show how the binding group influences photoluminescence (PL) and photovoltaic (PV) properties and stability for a series of surface ligands consisting of varying binding groups. These include ligands with both one and two potential binding groups, including zwitterionic molecules. We expected that zwitterionic ligands would display higher binding affinities and potentially improved trap state passivation, as the negatively charged part of the zwitterionic ligands can bind with positively charged undercoordinated Pb\(^{2+}\) ions of the perovskite film, while the positively charged group can fill in A-site vacancies. We find that zwitterions indeed lead to higher photoluminescence quantum yields (PLQYs) than monofunctional ligands.

**ET05.12.14**

**Electronic and Atomic Structure at the PCBM/CH\(_3\)NH\(_3\)/PbI\(_2\) Interface in Perovskite Solar Cells from *Ab Initio* Molecular Dynamics**

Rahi Khanal\(^1\), Nicholas Ayers\(^2\), Sheila Bruges\(^3\), Soumik Banerjee\(^3\) and Sanrat Choudhury\(^3\); 1University of Idaho, Moscow, Idaho, United States; 2School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington, United States.

In the perovskite solar cells, interfaces are crucial for efficient photovoltaic performance as they are responsible for both the injection and the transport of the charge carriers. Using *ab-initio* molecular dynamics simulations and density functional theory calculations, we have systematically determined the structural, electronic, and transport properties at a model CH\(_3\)NH\(_3\)/PbI\(_2\)/phenyl-C\(_6\)C\(_{41}\)-butyric acid methyl ester (PCBM) interface. The CH\(_3\)NH\(_3\)PbI\(_2\) is the photoactive layer while PCBM is the electron transport layer. We have observed that PCBM prefers to attach to the perovskite surface via ester moiety of PCBM molecule. Further, from the analysis of interatomic distances on several interface models, we found that the bonding at the interface and the stability of interface is sensitive to the chemical composition at the surface i.e. CH\(_3\)NH\(_3\)I vs. PbI\(_2\) surface terminations of the perovskite. Different preferences in bonding at the interface leads to the change in electronic and transport properties across two chemical terminations. Finally, we have shown that the stability of the interface can be increased by the introduction of certain types of defects at the perovskite surface, which may result in the better coverage of PCBM on the perovskite surface. However, such kind of defects could deteriorate the photovoltaic performance due to an increase in the potential barrier for the transport of charge across the interface.

**ET05.12.15**

**Impact of Anti-Solvents on the Structure and Optoelectronic Properties of Lead-Tin Mixed Perovskite Photovoltaics**

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Lead-tin (Pb-Sn) mixed perovskites have gained increasing attention due to the possibility of forming all solution processed tandem perovskite PVs (PPVs). One of the major obstacles towards enhancing the performance of the Pb-Sn PPVs has been the formation of high performing, pin hole free absorber layer. This is generally achieved using the anti-solvent treatment during the deposition of the perovskite layer, followed by thermal annealing (Saliba et al., Environ. Sci. 9, 1989). Another complication for mixed Pb-Sn PPVs is the fast oxidation of Sn\(^{2+}\) to Sn\(^{4+}\) which results low efficiencies due to p-type self-doping (Herz et al. Acc. Chem. Res. 49, 146). Various pathways have been investigated in decreasing this oxidation process with the most widely used being the incorporation of SnF\(_2\). This process however, while inhibiting the perovskite oxidation, generates Sn\(^{4+}\) ions in the system by the oxidation of Sn\(^{2+}\) to Sn\(^{4+}\) in SnF\(_2\), which are hardly removed from the system. Interestingly, extraction of Sn\(^{4+}\) from ionic mixtures, is reported to be most effective when using toluene as the extraction medium (Sargar et al. JCCS, 50, 841). Incidentally, toluene is one of the widely used aforementioned anti-solvents that enable high performing perovskite PVs (Jeon et al., Nat. Mater. 13, 897). However, there are no known studies reported on the effective removal of Sn\(^{4+}\) based on the anti-solvent route.

To investigate this, we discuss the impact of toluene and two other commonly used anti-solvents; anisole and chlorobenzene, on the triple cation Pb-Sn mixed perovskite system (Cs\(_{0.05}\)(FA\(_{0.83}\)MA\(_{0.17}\))\(_{0.95}\)Pb\(_{0.5}\)Sn\(_{0.5}\)I\(_3\)). We observe ~80% improvement in power conversion efficiency (with minimal optimization of the processing conditions) for the toluene treated Pb-Sn mixed perovskite with a champion efficiency of ~6% compared to chlorobenzene or anisole treated devices. This is reflected by enhancements in all the device parameters (open circuit voltage, short circuit current and fill factor). Terahertz mobility measurements carried out on the different anti-solvent treated perovskite films clearly indicate improvements in charge carrier lifetimes with toluene, where a slower decay time is observed. The impact on the use of the anti-solvent on the chemistry of the Pb-Sn mixed perovskite is further evident through grazing incidence wide angle X-ray spectroscopy where no noticeable differences in the diffraction spectra are evident for different anti-solvents. Based on the above we introduce a mechanism by which Sn\(^{4+}\) is extracted through toluene enabling a more purified Pb-Sn perovskite absorber layer growth.

The extraction of the Sn\(^{4+}\) by toluene is further strengthened by the studies on the, Cs\(_{0.05}\)(FA\(_{0.83}\)MA\(_{0.17}\))\(_{0.95}\)Pb\(_{0.5}\)(FA\(_{0.83}\)Ba\(_{0.17}\))\(_{0.93}\) system where the impact of the anti-solvent used is not as pronounced. Finally routes towards improving the Pb-Sn mixed perovskite performance which enables efficiencies approaching 15% is discussed.

**ET05.12.16**

**Perovskite Nanocrystals—Shape-Consolidated Synthesis to Self-Assembled Supercrystals with Tunable Optical Properties**

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Perovskite nanocrystals (NCs) are gaining increasing attention in many fields ranging from chemistry to physics and engineering owing to their extremely interesting properties such as high photoluminescence quantum yields, tunable optical bandgap, enhanced stability, large diffusion lengths and shape controllability. [1–4] In spite of the rapid progress in the synthesis of perovskite NCs, very few attempts have been made toward the self-assembly of perovskite NCs and understanding their coupled optical properties. Shape-consolidated synthesis and their self-assembly into ordered superlattices has emerged as a powerful tool for tailoring the nanoscale optical properties. Such coupled optical and electronic properties can be utilized for the development of interesting nanomaterials.
of novel optoelectronic devices.

In this talk, I will present a one-pot shape-controlled synthesis of highly crystalline and monodisperse CsPbX3 (X=Cl, Br and I) perovskite NCs of various morphologies such as nanocubes, nanoplates (NPs), nanowires (NWs) and nanorods (NRs) starting from their precursor powders. [2-5] The morphology of perovskite NCs can be controlled by means of simple chemistry such as Cs/Pb precursor ratios, reaction time and ligand concentration. We discovered that the perovskite NCs spontaneously self-assemble into nanowires through oriented-attachment or supercrystals (SCs) depending on the reaction conditions. The optical bandgap of the perovskite NCs as well as SCs can be controlled over the entire visible range by varying the halide (Cl, Br, and I) composition. Our work not only provides a facile method for the shape-control of monodisperse perovskite NCs and their self-assembly, but also expands our current understanding of the morphology-dependent optical properties, and open new avenues for the fabrication of highly ordered architectures using perovskite NC building blocks for future optical and optoelectronic devices.

References


ET05.12.17 Origins of Phase Heterogeneity in 2D Lead Halide Perovskite Films Explored Through Intermediate Crystallization and Growth Trajectories Clayton J. Dahlman1, Ryan A. DeCrescent1, Navene Venkatesan, Jon A. Schuller2 and Michael L. Chabinyc1; 1Materials, University of California, Santa Barbara, Santa Barbara, California, United States; 2Electrical and Computer Engineering, University of California, Santa Barbara, Santa Barbara, California, United States.

2D layered lead halide perovskites approach the precise optoelectronic efficiencies of 3D perovskites while allowing for tunable optical and electronic properties and greater stability to environmental conditions. The ratio between AMX perovskite layers and alkylammonium spacer layers (the ‘n-value’ in (RNH3)2An-1MnX3n+1) can be tuned to alter the bandgap and other properties through confinement effects. However, this additional compositional degree of freedom presents a challenge to control microstructural homogeneity in thin-films. Despite thorough characterization of single-crystal Ruddlesden-Popper lead halides with various spacer cations and stoichiometries, the microstructure of thin films remains an active area of exploration. Several accounts have demonstrated the phase impurity of Ruddlesden-Popper thin films, revealing a mixture of ‘n-values’ along with variations in grain texturing and device performance. Emission energies of Ruddlesden-Popper thin films also diverge from single-crystal studies, showing red-shifts in photoluminescence of thin films. We have performed a fundamental study to observe grain growth of (C4H9NH3)2PbI2 (C4H9NH3)2PbBr2 thin films via in situ video, PL and XRD of drop-cast films. Film growth proceeds through a distinct C4H9NH3+ rich, rich solvated structure before forming smaller grains of C4H9NH3+ rich perovskite structures upon solvent evaporation, similar to crystallization studies of 3D MAPbI3. The early formation of PbI2-solvates appears to sequester CH3NH3+, skewing the effective ratio of alkylammonium ions during later crystallization and yielding compositional heterogeneity in the film. Optical and structural transformations are observed in each local microstructure upon film annealing (i.e. loss of coordinated solvent), supporting the role of the solvate intermediate in generating phase heterogeneity. Furthermore, PL at ‘single crystal’ energies is observed in directly-crystallized perovskite regions throughout growth, suggesting that ‘thin film’ states are also impacted by the solvate intermediate. These results imply that intermediate solvate-PbI2 crystallization impede phase-pure Ruddlesden-Popper growth, and may contribute to observed red-shifts of thin film photoluminescence. Thus, a selection of highly basic solvents is explored to prevent growth of intermediate solvate-PbI2 phases, revealing a clear trajectory to tune phase-purity and optoelectronic properties of polycrystalline thin-film 2D perovskites.

ET05.12.18 Synthesis, Fundamental Properties and Nanostructures of a New Lead-Free Perovskites Rb2SbCl5 Meiying Leng1,2, Matthew P. Hautzinger1, Yongping Fu1, Ilia Guzei1, Zhifang Tan2, Jinghui Li2, Jiang Tang2 and Song Jin1; 1University of Wisconsin Madison, Madison, Wisconsin, United States; 2Wuhan national laboratory for optoelectronics, Huazhong University of Science & Technology, Wuhan, China.

Lead halide perovskites have become known for their exceptional optical properties and potential for application in photovoltaics and light emission devices. However, the toxicity of soluble Pb2+ hinders commercialization. Non-toxic, group VA elements, such as Bi3+ and Sb3+, contain ns2 valence electrons and are isoelectronic with Pb2+ and Sn2+. In spite of the inability to form 3D network perovskite based on charge balancing arguments, group VA metal halides show modest performance in solar cells and as quantum dots for light emission which merits continued investigation. Here we report a newly discovered lead-free perovskite, Rb2SbCl5. The crystal structure consists of two OD bonding motifs in the same crystal structure that are charge balanced and interceded by Rb+ cations. It shows a bright, broad emission at 542 nm (FWHM = 120 nm), which may be an indication of a self-trapped exciton or result of emission from the multiple bonding motifs in the materials. Hexagonal nanoplates are further grown prepared by a facile dissolution-recrystallization method and they display strong RT photoluminescence. Furthermore, the photoluminescence (PL) peaks of Rb2SbCl5X48 nanoplates can be easily tuned from 542 to 630 nm by changing the ratio of Cl/Br. These materials are promising lead-free metal halides for optoelectronic applications, as well as for fundamental study of solid-state chemistry and physics of perovskites.

ET05.12.19 Pressure-Induced Phase Transformation and Bandgap Engineering of Formamidinium Lead Iodide Perovskite Nanocrystals Hua Zhu1, Tong Cai1, Meiyan Que1, Jeong-Pil Song1, Brenda M. Rubenstein1, Zhongwu Wang2 and Ou Chen1; 1Brown University, Providence, Rhode Island, United States; 2Cornell University, Ithaca, New York, United States.

Formamidinium lead halides (FAPX3, X=Cl, Br, I) perovskite materials have recently drawn an increased amount of attention owing to their superior optoelectronic properties and enhanced material stability as compared to their methylammonium-based (MA-based) analogues. Herein, we report a study of pressure-induced structural and optical evolution of FAPbX3 hybrid organicinorganic perovskite nanocrystals (NCs) using a synchrotron-based X-ray scattering technique coupled with in situ absorption and photoluminescence (PL) spectroscopies. As a result of their unique structural stability and soft nature, FAPbX3 NCs exhibit a wide range of bandgap tunability (1.44 eV – 2.17 eV) as a function of pressure (0 – 13.4 GPa). The study presented here not only provides an efficient and chemically orthogonal means to controllably engineer the bandgap of FAPbX3 NCs using pressure, but more importantly...
Methylammonium lead iodide perovskite can be functionalized by ammonium benzoic acids, yielding carboxylic acid groups capable of undergoing subsequent surface reactions. The ammonium salts of 4-aminobenzoic acid, 5-aminoisophthalic acid, and 3,3′-diaminobenzoic anhydride were synthesized and substituted onto the surface using previously explored techniques. The mechanism of substitution was elucidated via XPS. The molecular orientation was determined via infrared reflection absorption spectroscopy. The anhydride experiments were used specifically to examine the orientation due to the rigidity of the anhydride on the surface relative to the carboxylic acids in the other molecules. The carboxylic acids were also found to be useful chemical hooks in this system for atomic layer deposition and has been explored using organometallic reagents. This technique is a powerful tool, enabling an atom-and-bond level understanding to be applied to the protection of perovskite semiconductor materials.
8:00 AM ET05.13.01
Highly Emitting Blue Inorganic Halide Perovskite Quantum Dots and Nanocrystals Jianjun Tian; University of Science and Technology Beijing, Beijing, China.

All-inorganic perovskite cesium lead halide quantum dots (QDs) have been widely investigated as promising materials for optoelectronic application, because of its outstanding photoluminescence (PL) properties and benefits from quantum effects. Although QDs with full-spectra visible emission have been synthesized for years, the PL quantum yield (PLQY) of pure blue emitting QDs still stays at low level in contrast to their green or red emitting counterparts. Herein, we obtained core-shell structured cubic CsPbBr3@amorphous CsPbBr3 (A-CsPbBr3) perovskite QDs via a facile hot injection method and centrifugation process. The core/shell structure QDs showed a record pure blue emission PLQY of 84%, which is much higher than that of blue emitting cubic CsPbBr3 QDs and CsPbBr3Cl1-x QDs. Furthermore, a blue emitting QDs-assisted-LED with bright pure blue emission was prepared and illustrated the core-shell QDs' promising prospect in optoelectrical application. Recently, another work shows the transformation of the crystal structure and remarkably high crystallinity of the γ-crystals, leading to the record blue PLQY of 91% at 480 nm.

8:15 AM ET05.13.02
Spontaneous Iodide Loss from 2D Perovskite Single Crystals N-Dopes 2D Perovskites Lianfeng Zhao1, He Tian2, Scott Silver1, Antoine Kahn1, Tian-Ling Ren2 and Barry P. Rand1; 1Princeton University, Princeton, New Jersey, United States, 2Tsinghua University, Beijing, China.

Despite the demonstrated high efficiency of perovskite solar cells and light emitting devices, the understanding of the intrinsic stability of perovskites is far from complete. In this work, using an ultrasensitive, exfoliated 2D perovskite single-crystal sheet/graphene heterostructure device, we reveal spontaneous iodide loss as an important degradation pathway of 2D perovskite single crystals, which acts as a donor and n-dopes the 2D perovskite semiconductor, generating positively charged iodide vacancies. First, single crystals of 2D perovskites are exfoliated to a thin sheet of ~55 nm, and a 2D perovskite/graphene heterostructure-based field-effect transistor is employed to monitor the 2D perovskite degradation. We show that the 2D perovskite thin crystal sheet is intrinsically unstable, leading to a continuous shift of the Fermi level of graphene with respect of the Dirac point position observed in \( L_\text{F} \) vs. \( V_\text{G} \) curves. Moreover, the degradation is accelerated by light illumination. The mechanism underlying this effect is the spontaneous loss of iodide, which is confirmed by cross-sectional scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), ultraviolet photoelectron spectroscopy (UPS), and Kelvin probe measurements. The release of iodide generates iodide vacancies, which induce an n-type doping of the perovskite, shifting the Fermi level of both perovskite and graphene up. Furthermore, we show that a graphene cover on the perovskite thin crystal sheet can improve perovskite stability by preventing iodide loss. An ultra-stable phototransistor based on the graphene/2D perovskite/graphene structure is demonstrated, which shows almost no degradation over 75 days.

8:30 AM ET05.13.03
Origin of Green-Light Emission of the Zero-Dimensional Bromide Perovskite CsPbBr3 Young-Kwang Jung1, Ji-Sang Park2 and Aron Walsh1-3; 1Yonsei University, Seoul, Korea (the Republic of); 2Imperial College London, London, United Kingdom.

Halide perovskite families have been widely studied for photovoltaics [1-2] due to their unique optoelectronic properties, but recently, they are being studied for light-emitting applications [3]. Beyond regular perovskites based on a corner-sharing octahedral network, CsPbBr3, which is called as zero-dimensional perovskite, is getting attention because of its highly-efficient green light luminescence [4]. The reported band gap of CsPbBr3 of 3.9 eV is in the ultraviolet (UV) region, thus green light emission in this material cannot be due to its intrinsic band gap. The origin of the green light emission has not clarified and two hypotheses have been suggested to explain this phenomenon: (i) CsPbBr3 phase impurities within the material and (ii) luminescent defect states within the band gap of CsPbBr3. We investigate the chemical and physical properties of the CsPbBr3, based on first-principles simulations, including a thorough analysis within the modern theory of defect formation [5], from which we predict the origin of the green light emission.}


8:45 AM ET05.13.04
Resonantly Generating Multiple Excitons with Multiple Below-Band-Gap Photons in Metal Halide Perovskite Nanocrystals Aurora Manzi, Yu Tong, Julius Feucht, En-Ping Yao, Lakshminarayana Polavarapu, Alexander S. Urban and Jochen Feldmann; LMU Munich, Munich, Germany.

Multiple exciton generation (MEG) is a process that addresses the conversion of highly energetic photons by using their excess energy to promote additional electrons to the conduction band. However, this process requires that the energy of the exciting photon is at least twice the band-gap of the semiconductor, which is hardly achievable with visible light. In our studies we have shown that it is possible to use multiple low-energy photons to efficiently generate multiple excitons in metal halide perovskite nanocrystals. Additionally, high-order absorption processes, deviating from the expected two-photon absorption, can be observed at very specific energetic positions. We could associate these specific energies to multiples of the semiconductor band-gap energy. In such a way, we have developed a method by means of which we were able to describe this effect as a resonant behaviour between multi-photon absorption (MPA) and MEG, which has never been seen before.

Interestingly, the resonance effect between MPA and MEG could only be observed once the perovskites were assembled in an orderly fashion, forming
supercrystals. This phenomenon can be attributed to the electronic coupling given by the close-packed arrangement of the individual nanocrystals that reduces the incidence of Auger recombination, which represents the main opponent of the survival of multiple excitons. When the supercrystal geometry is kept, the chemical composition of the perovskites can be varied to tune the energetic position of the MPA-MEG resonances. We have in fact demonstrated that the same effect can be obtained for different halides (X) in CsPbX3 perovskites.

Currently lead based all-inorganic cesium lead halide perovskite nanocrystals (NCs), have been shown great potential for high-performance light-emitting diodes (LEDs) and solar cells owing to their excellent optical properties and inexpensive synthesis process. Here, we successfully doped hetrovalent Bi3+ ion into the lattices of CsPbBr3 perovskite NCs through a hot-injection method. The Bi3+ cation has been chosen as the dopant by reason of its similar ionic radius to preserve the integrity of perovskite structure. We achieved maximum 6.93% Bi doping which is considerably higher as compared to those achieved in previous reports via hot injection method.

It was found that by increasing the Bi3+ ion concentration, the morphology of CsPbBr3 NCs changed from cubic to hexagonal and precisely tune the band structure and photoluminescence (PL) of host CsPbBr3 NCs by inducing the trap states within the band gap. Time-resolved photoluminescence (TRPL) spectroscopy revealed that Bi3+ ion doping significantly enhance the lifetime of charge carriers. This work indicates that Bi doped CsPbBr3 NCs occurs better optical properties than pure CsPbBr3 NCs and can be a promising material for high-performance perovskite LEDs.
Here, we explore the application of a phosphine oxide (R,P=O) to synthesise cesium lead bromide perovskite nanocrystals, replacing the labile amine ligand and mirroring the R−O group required in the macroscale synthesis. The synthetic route we present provides us with exceptionally high yields of very monodisperse particles, which are not only highly emissive, but can also be synthesised in air, obviating the need for laborious solvent degassing, and complicated oxygen and moisture free techniques.

Through a comparison of both synthetic routes, we observe improved stability of the R,P=O nanocrystals to washing. Additionally, we are able to expand this synthetic protocol to a variety of other anions and cations, as well as being able to replace the carboxylic acid with either phosphonic or phosphinic acids, demonstrating the robustness and versatility of this technique. By using nuclear magnetic resonance and x-ray photoelectron spectroscopy we are able to investigate the surface of our nanoparticles and determine the cause of increased stability and show the importance of phosphine oxide in the synthesis of perovskite nanocrystals.

10:30 AM ET05.13.09
Exciton Dynamics in Quantum Confined CsPbBr3 Nanoplatelets Moritz Granich1,2, Bernhard J. Bohn1,2, Yu Tong1,2, Lakshminarayana Polavarapu1,2, Alexander S. Urban1,2 and Jochen Feldmann1,2; 1Chair for Photonics and Optoelectronics, Department of Physics and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, Munich, Germany; 2Nanosystems Initiative Munich (NIM), Munich, Germany.

In contrast to bulk perovskite films, recent reports have shown that in perovskite nanocrystals the excitonic absorption onset and photoluminescence (PL) peak exhibit a blue shift due to quantum confinement when their size is in at least one dimension approaches the exciton Bohr radius of the respective perovskite composition.[1] For decreasing thickness of organic-inorganic perovskite nanoplatelets – separated by centrifugation – increasing exciton binding energies and decreasing PL decay times have been observed.[2] Recently, we have developed a new method which enables the direct synthesis of quantum-confined inorganic CsPbBr3 nanoplatelets of uniform thickness with an atomic layer precision. These nanoplatelets are characterized by a highly efficient light-emission in the blue spectral range. Here, transient absorption spectroscopy is applied to CsPbBr3 nanoplatelets of different thickness varying from two to six monolayers to gain additional insight into confinement effects on the dominant exciton dynamics in these systems. A special focus is put on the fast exciton-exciton annihilation process, which plays an increasingly important role for higher excitation powers.


10:45 AM ET05.13.10

Lead halide perovskites AP$\text{BX}_3$ [A = methylammonium (MA), formamidinium (FA), and Cs, X=I, Br, and Cl] has excellent properties suitable for optical devices. The halide perovskites have been extensively studied on single crystals and thin films. Moreover, the synthesis of high-quality nanocrystals has been developed in recent years [1]. Since excitons are strongly confined within nanocrystals, optical responses depends on the size of the nanocrystals. One advantage of nanocrystals is that a spatially confined exciton enhances the radiative recombination rate, and then nanocrystals exhibit high photoluminescence quantum yields (PLQYs) even at room temperature. On the contrary, such spatial confinement works negatively for multiple excitons leading to a decrease in PLQYs as the non-radiative Auger recombination rate of multiple excitons is enhanced [2, 3]. Therefore, it is necessary to elucidate the impact of spatial confinement on the radiative processes for nanocrystal device applications. In particular, size-dependent PL dynamics of nanocrystals should be elucidated.

In this study, we report on the size-dependent PL dynamics of perovskite nanocrystals revealed by single dot spectroscopy. The samples used in this study were two types of perovskite nanocrystals with different A site cations (FAPbBr3 and CsPbBr3), which were prepared by hot injection method. Time-resolved and spectrally resolved PL measurements were performed for individual single nanocrystals. Single-dot spectroscopy enables us to analyze optical properties for each individual nanocrystal that cannot be obtained in ensemble nanocrystal measurements. From the obtained results, we clarified that those nanocrystals with larger absorption cross sections exhibit longer exciton lifetimes. Since this tendency was observed with both FAPbBr3 and CsPbBr3 nanocrystals, it was suggested that spatial confinement is the dominant factor determining the exciton lifetime. Furthermore, since the lifetime of a single exciton generation is a major factor determining PLQYs, the size dependence of PLQYs is analyzed from the fraction of on-state and off-state in PL blinking behavior. These nanocrystal size dependences of PL dynamics for excitons, trions and multiple excitons provide important insights for improving the performance of nanocrystal-based devices.

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11:00 AM ET05.13.11
Contactless Measurements of Lattice and Photogenerated Charged Carrier Dynamics in Organic-Inorganic Hybrid Perovskite Single Crystals Jian Wang1,2, Elaheh Motaharinia1, Lakshmi N. Murthy1, Marissa N. Higgins1, Diego Barrera1, Trey Daunis1, Yangzi Zheng3, Anton Malko1, Fernando Ely4,5, Manuel Quevedo-Lopez2, Mark Lee2 and Julia W. Hsu1; 1Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas, United States; 2Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, Munich, Germany; 3Physics, The University of Texas at Dallas, Richardson, Texas, United States; 4Centro de Tecnologia da Informação Renato Archer, Santa Monica, Brazil.

Hybrid organic-inorganic lead halide perovskites have revolutionized optoelectronic applications, including solar cells, light-emitting diodes, and photodiode detectors. Despite the rapid advances in applications, fundamental understanding of these remarkable materials has just begun. While most applications use thin films that contain multiple grains, high-quality single crystals that contain minimal defects are pertinent to understanding the fundamental properties, hence the limit of attainable optoelectronic performance. However, depositing the electrical contacts on fragile single crystals can often alter them, e.g. by inducing doping. Here we present two contactless techniques, far-infrared (FIR) reflectance and surface photovoltage (SPV) measurements, to probe lattice dynamics and photogenerated carrier dynamics, respectively, on high-quality methylammonium lead bromide (MAPbBr3) single crystals. FIR reflectance shows three coherent infrared-active phonon modes between 40 to 200 cm$^{-1}$ that result in restrahlen bands with much higher peak reflectance than has been previously reported for single crystal MAPbBr3. The phonon mode strength and damping are comparable to what is commonly observed in classical oxide perovskite single crystals, suggesting phonon coherence across macroscopic scale and that the crystal likely contains few grain boundaries or stacking faults. However, these crystals can still contain point defects, which contribute to SPV signals. By performing SPV measurements, to probe lattice dynamics and photogenerated carrier dynamics, respectively, on high-quality methylammonium lead bromide (MAPbBr3) single crystals.
measurements over different spectral ranges, we are able to separate the effects of surface and bulk defects on the recombination dynamics of photocathode-driven charged carriers. We further apply SPV measurements to obtain the minority carrier (electron) diffusion length for the MAPbBr$_3$ crystal.

This study demonstrates that both FIR reflectance and SPV measurements provide useful electromagnetic response information on the halide perovskite single crystal properties.

11:15 AM ET05.13.12

Tetragonal to Cubic Phase Transition in FA$_x$Cs$_{1-x}$PbI$_{3-y}$Br$_y$—Temperature Dependence and Impact on Band Gap

Julien Barrier$^1$, Aryeh Gold-Parker$^1$, Eli Wolf$^2$, Rachel E. Beal$^1$, Michael D. McGehee$^3$ and Michael F. Toney$^1$; $^1$SSRL Materials Science Division, SLAC National Accelerator Laboratory, Menlo Park, California, United States; $^2$Department of Chemistry, Stanford University, Stanford, California, United States; $^3$Department of Applied Physics, Stanford University, Stanford, California, United States; $^4$Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; $^5$Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States.

In the pursuit of efficient tandem solar cells, high band-gap photovoltaic absorbers are required for top cells. Hybrid perovskites are promising candidates, as their band gaps can be widely tuned via compositional adjustments. Specifically, perovskites of the form FA$_x$Cs$_{1-x}$PbI$_{3-y}$Br$_y$ have shown high device efficiencies as well as high band gaps suitable for tandem applications [1]. In this family of perovskites, we have observed a tetragonal-cubic phase transition that is coincident with a change in the temperature coefficient of the band gap and also occurs within solar cell operating temperatures. It has been suggested [2] that the phase transition may impact light induced phase segregation, which has been identified as a major concern that lowers operating voltages in mixed cation perovskite solar cells [1]. Thus, it is key to understand the phase behavior of this family of perovskites, as well as the impact of structural changes on electronic properties.

We explore here a wide compositional space of FA$_x$Cs$_{1-x}$PbI$_{3-y}$Br$_y$ thin films with temperature-dependent synchrotron X-ray diffraction. At room temperature, many of these compositions exhibit tetragonal peaks that we have indexed to the P4/mmm space group, corresponding to concerted octahedral tilting about the c axis of the perovskite crystal structure. This is distinct from tetragonal MAPbI$_3$, which has alternating tilt directions about the c axis corresponding to the I4/mcm space group. We compute the structure factors of a number of Bragg peaks that allow us to model the average octahedral tilt angle as a function of the temperature. Within the FA$_x$Cs$_{1-x}$PbI$_{3-y}$Br$_y$ family, we show how varying the composition affects the phase transition temperature and we present a room temperature phase diagram. Additionally, we show that the temperature coefficient of the band gap presents a discontinuity at the phase transition temperature. This effect is related to band gap tuning observed in mixed Pb-Sn perovskites, which share the same tetragonal space group [3]. This work establishes a phase diagram that may help interpret photo-stability and will enable better prediction of band gaps in this family of hybrid perovskites.

References


11:30 AM ET05.13.13

Phase Transition and Anion Exchange in Lead Halide Perovskites

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Lead-halide perovskites are a family of semiconductor materials with excellent optoelectronic properties ideally suited for next-generation photovoltaic and light-emitting applications. Particularly, inorganic perovskites CsPbX$_3$ are drawing increasing research interests because of their better stability. There are rich structural phase transitions in the inorganic perovskites owing to their soft and dynamical ionic lattice. However, the fundamental understandings of intrinsic phase transition mechanism are still elusive. In this talk, I will focus on the systematical study of the phase transition between a non-perovskite and a perovskite phase using single-crystal CsPbI$_3$ nanowires platform. The non-perovskite phase with a large bandgap and poor photoactivity can be thermal-driven transformed to a meta-stable perovskite phase with a decreasing bandgap and excellent optoelectronic properties. Moisture introduces vacancy in the crystal lattice and lowers the kinetic barrier from perovskite phase to non-perovskite phase. We further realize robust thermochromic solar cells for smart photovoltaic window applications via stable, controllable and reversible phase transition. Another feature of the soft ionic lattice is facile ion migration. Anion exchange chemistry was demonstrated in CsPbX$_3$ nanostructures with high PLQY throughout the exchange reaction. Via developing a novel localized anion exchange, we demonstrate spatially resolved multi-color CsPbX$_3$ nanowire heterojunctions. These perovskite heterojunctions show tunable photoluminescence over the entire visible spectrum with high resolution down to 500 nm, which represent key building blocks for high-resolution displays. Moreover, the intrinsic solid-solid anion exchange dynamics can be resolved in these perovskite hetero-junction nanowires through non-destructive optical methods. These fundamental understandings can offer guidelines for engineering the perovskite materials with novel functional devices.

11:45 AM ET05.13.14

Understanding and Improving the Surface Ligand Capping of Cesium Lead Bromide Nanocrystals

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Colloidal lead halide perovskite nanocrystals (NCS) have recently emerged as versatile photonic sources. Their processing and luminescent properties are largely governed by the lability of their surface structure, that is the surface regions of the NC core and ligand shell. In this study and using CsPbBr$_3$ NCS as a model system,[1] we model the nanocrystal surface structure and its effect on the emergence of the trap states using density functional theory. We then rationalize the typically observed effects of the surface treatment and aging on the luminescent characteristics. We illustrate and discuss the utility of common elemental analysis methods, namely inductively-coupled plasma – optical emission spectrometry and X-ray photoelectron spectroscopy, for elucidating the chemical changes induced by surface treatments. We propose a strategy for healing the surface trapping states and for improving the colloidal stability by the combined treatment with didodecyldimethyl ammonium bromide and lead bromide and validate this approach experimentally. This simple procedure results in robust colloids, which are both highly pure and exhibit high photoluminescence quantum yields of up to 95-100%.

[1] manuscript submitted
The recently re-emerged two-dimensional organic-inorganic hybrid perovskites (2DHPs) are solution processable semiconductors exhibiting strong quantum and dielectric confinement effects, as well as excellent luminescence properties. However, even some of the most fundamental optical properties, especially the complex refractive index (RI), currently are unknown for 2DHP single crystals. As for any optoelectronic materials, refractive index is crucially important since: 1) The real part (n) encodes the phase velocity of light, which, e.g., underpins the resonant condition of a laser cavity, and 2) the imaginary part (k) dictates absorption, which is key for optimizing the thickness of a solar cell. Herein, using a newly-developed dielectric-coating based technique, we determine the complex, anisotropic RI for 2DHP single crystals with various perovskite-layer thicknesses and different types of organic spacers. We found 2DHPs that are only one or two perovskite layers in thickness exhibit negative permittivity due to strong in-plane exciton resonances, but positive permittivity owing to substantially weaker out-of-plane exciton resonances. The extreme excitonic anisotropy in the periodic 2DHPs leads to a natural hyperbolic dispersion in the visible range, which has been previously achieved only with artificial metamaterials. Our observation opens new possibilities in enhanced emission & absorption properties, nonlinear optics, and enhanced light-matter interactions.

**1:45 PM ET05.14.02**

**Templating Hybrid Perovskite Growth for Highly Efficient Light-Emitting and Photovoltaic Devices**

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Hybrid halide perovskites, extensively used in the field of optoelectronics, are a class of materials extremely promising for their excellent properties combined with the mild synthetic protocols. Mainly used in solar cells and light emitting diodes, perovskites are formed from solution by self-assembly of precursors. The resulting soft material is often unable to express its ideal potential, due to unsuitable morphology or elevated density of electronic defects as a consequence of the low-temperature processing. Based on our previous findings on the interaction between perovskite precursors and additives, we here explore the use of a tailored biopolymer, starch, as templating agent for the growth of formamidinium (FA)- and methylammonium (MA)-based triiodide perovskite films. The presence of the macromolecule brings the enormous technological advantage of allowing the deposition of the perovskite layer with a one-step method, avoiding solvent dripping or two-steps method. Furthermore, it allows a fine tuning of the solution viscosity (making the solution more compatible with the substrate), providing a layer-by-layer coating of the perovskite film, allowing continuous adjustment of the film thickness. The extreme excitonic anisotropy in the periodic 2DHPs leads to a natural hyperbolic dispersion in the visible range, which has been previously achieved only with artificial metamaterials. Our observation opens new possibilities in enhanced emission & absorption properties, nonlinear optics, and enhanced light-matter interactions.
exciton binding energy than 3D perovskites. However, the complexity in the wet-chemical processes make the synthesis of high purity homologous 2D perovskites still a big issue. In addition, the fundamental mechanism of the nucleation and growth of the phase transition and the rate of the emission in 2D RPP with different layered perovskite compounds is still lacking. In this direction, we grew a high purity micrometer-sized single crystal 2D RPP (BA$_2$MA$_3$,PbBr$_{3n+1}$, n=1, 2, 3) which cover whole visible light range by using slow evaporation at a constant-temperature (SECT) solution growth. Via the XRD, spectral mapping, and fluorescence lifetime mapping measurements, the large sized 2D RPP crystals show well crystallinity and highly phase purity. Furthermore, due to the pyramid step-like structure, we obtain cavity-free lasing behavior with around 3.7 $\mu$m/cm$^2$ threshold from these homologous large sized crystals. Also, with high pure phase crystal, we can identify the carrier dynamics before and after phase transition directly without defect state induced effect. Our result demonstrates that solution growth homologous organic-inorganic hybrid 2D perovskite single crystals open up a new window as a promising candidate for optoelectronic devices. (This work has been published in Nano Lett. 2018, 18, 3221–3228)

2:15 PM ET05.14.04
Hybrid Perovskite Heterostructures for Efficient LEDs—Luminescence Performance, Carrier Kinetics and Optical Modeling
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Perovskite-based optoelectronic devices have gained significant attention due to their remarkable performance and low processing cost, particularly for solar cells. However, for perovskite light-emitting diodes (LEDs), non-radiative charge carrier recombination has limited electroluminescence (EL) efficiency. Here we demonstrate perovskite-polymer bulk heterostructure LEDs exhibiting record-high external quantum efficiencies (EQEs) exceeding 20%, comparable with the best solution-processed OLEDs and quantum-dot LEDs. This performance is achieved with an emissive layer comprising quasi-2D and 3D perovskites and an insulating polymer.

Transient optical spectroscopy reveals that photogenerated excitations at the quasi-2D perovskite component migrate to lower-energy sites within 1 ps. The dominant component of the photoluminescence (PL) is primarily dimolecular and is characteristic of the 3D regions. From the near-unity PL quantum efficiencies and transient kinetics of the emissive layer with and without charge-transport contacts, we find non-radiative recombination pathways to be effectively eliminated. Light outcoupling from planar LEDs, as used in OLED displays, generally limits EQE to 20-30%, and we model our reported EL efficiency of over 20% in the forward direction to indicate the internal quantum efficiency (IQE) to be close to 100%. Together with the low drive voltages needed to achieve useful photon fluxes (2-3 V for 0.1-1 mA/cm^2), these results establish that perovskite-based LEDs have significant potential for light-emitting applications. In general, the ideal luminescence performance we observe is of critical importance for realizing perovskite optoelectronics operating near the radiative limits.

We also present some related results from our group and collaborating groups, on luminescent perovskites for LEDs and photovoltaics.

2:30 PM ET05.14.05
The Application of 2D Materials in Perovskite Solar Cells
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We report a cost-effect approach for improving the performance of perovskite solar cells by using novel high-mobility 2-dimensional materials. The efficiency of perovskite solar cells can be substantially enhanced when 2-dimensional material flakes are coated on the perovskite grain boundaries. The flakes can conduct hole currents efficiently from grain boundaries to hole transport layers in the devices and lead to efficiency enhancements that increase with increasing hole mobilities of the flakes. The results indicate that perovskite grain boundaries are electrically benign and even favorable for photovoltaic performance if accumulated charges around them are conducted out by high mobility hole transport materials.

2:45 PM ET05.14.06
Photo-Induced Lattice Symmetry Improvement in Organic Lead Halide Perovskite and Its Beneficial Effect on Charge-Transfer Dynamics
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The hybrid organic lead halide perovskites based on mixed-cations and -anions have been considered as an outstanding composition to achieve high efficiency with long-term stability of perovskite solar cells (PSCs). In this study, the effect of light on the crystal structure of perovskites employing triple cations and double halides was investigated and correlated to the charge-transfer properties. Under the continuous photon excitation, a gradual increase in photoluminescence was observed from the perovskite film, coupled with a minute red-shift. Furthermore, the continuous light soaking induced a gradual peak shift toward lower angle in the X-ray diffraction pattern of the perovskite, strongly suggesting a photo-induced structural response. Notably, a lattice expansion occurred in a certain preferred orientation, which exerted an influence on the crystal symmetry. The trap density of a complete PSC near the radiative limits.

We also present some related results from our group and collaborating groups, on luminescent perovskites for LEDs and photovoltaics.

3:00 PM BREAK

3:30 PM ET05.14.07
Porous Fractals of MAPbI$_3$ Perovskite—Characterization of Crystal Grain Formation by Irreversible Diffusion-Limited Aggregation
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Isopropanol solution based methylammonium lead triiodide (MAPbI$_3$) is studied during the crystallization process. The crystal growth starts in an unstable suspension far from equilibrium by forming distinct dendritic pattern and terminates with aggregation of stable cubic crystalline grains into fractal clusters. Using transmission electron microscopy (TEM), the time evolution of a newly mixed suspension was studied over a period of two weeks at room temperature and a sequence of the morphological changes was observed. The crystallization process started with single dendritic growth exhibiting branches at 90 degrees angles to one another. After 4 hours, a multi-dendritic growth pattern and a transformation into small crystalline quantum dots were observed. After a week, clusters of crystal grains were formed into a fractal pattern and these patterns appear to be stable also during the second week. Electron and x-ray diffraction revealed the crystallinity of the quantum dots and the clusters of micrometer-sized crystals. Scanning transmission electron microscopy (STEM) together with energy dispersive X-ray spectroscopy (EDS) showed that newly formed large grains, from a one hour old solution, displayed a core-shell structure with higher percentage of Pb atoms as compared to iodine at the surface. In, the inner core of the grains the percentage of iodine was slightly higher. The electron diffraction (ED) scan over the newly formed grains revealed a polycrystalline surface whereas the inner part had a single crystal pattern. The same solution, now one-week-old, contained grains with only single crystal patterns in the ED scan and showed no core-shell character or polycrystalline surface. The measured percentage of iodine atoms compared to lead was 2:1 throughout the cross section, which is a quantitative value within the measurement. It can be concluded from these measurements that the suspension approaches higher crystallinity of the perovskite grains in an irreversible process, where the perovskite grains are insoluble in isopropanol. The perovskite material has also been characterized
with scanning electron microscopy (SEM) and photoluminescence (PL) mapping where both techniques showed a very porous crystalline material. The PL mapping revealed two peaks at 730 and 760 nm for a thin film spin coated from a newly mixed solution, while a film deposited from a one week old solution showed three peaks, the last one at 830 nm. Because of the high crystallinity, it is suggested that all three peaks are due to band-to-band transitions and not due to localized states. These data will be analyzed further; however, the results contain information of the content of quantum dots versus larger crystals, as well as displaying emission intensity variations at different positions of the grains. The purpose with this project is to understand these phenomena of crystal growth. A new mesoporous perovskite material has been designed for optoelectronic purposes.

3:45 PM ET05.14.08
Energy Level Alignment at Halide Perovskite Interfaces
Philipp Schulz; IPVF, Centre National de la Recherche Scientifique, Palaiseau, France.

The ongoing development of halide perovskite (HaP) based optoelectronics has revealed that the numerous interfaces in the device play a crucial role for device functionality, efficiency and stability.1 Importantly, many critical material and interfacial properties are still poorly understood and difficult to assess, a deficiency that often limits efforts to improve the performance.2 I will present our most recent results exploring the mechanisms by which organic semiconductor films, transition metal oxides, and carbon nanotube (CNT) interlayers enable or suppress charge transfer to an adjacent HaP semiconductor film. We use photoemission, X-ray absorption, and transient optical spectroscopy to probe the energy level alignment and exchange of charge carriers between a set of various lead halide based perovskite films and different charge transport layers. Therein, we show that ground state charge transfer between perovskite and a CNT layer can lead to band bending in the transport layer beneficial for charge extraction.3 Hence, in one example an integrated thin CNT interlayer facilitates rapid charge carrier collection and improves the performance of respective solar cells.4 In contrast to this observation, band bending induced in the perovskite film by the charge transport material such as high work function oxides or interface defects induced by the oxide formation process can be detrimental for charge carrier collection and thus impede the functionality of respective devices.5

After examining the recent key developments in chemical and electronic structure characterization of HaPs, I will iterate the next steps towards interlayer tailoring and analysis.


4:00 PM ET05.14.09
Surface Molecular Doping of Metal Oxide Nanocrystals for Interface Engineering of Perovskite Solar Cells
Zhuanging He1,2, Wei Chen1,2, Bao Tu1 and Yinghui Wu1,2; 1Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China; 2Shenzhen Key Laboratory of Full Spectral Solar Electricity Generation (FSSEG), Shenzhen, China.

As a stable and promising hole transport layer (HTL) of planar perovskite solar cells (PSCs), the conductivity of the intrinsic NiO synthesized by solution process is nevertheless low and its hole mobility is also decreased by the nickel vacancies at deep gap states. In contrast to successful cesium or copper doping in NiO nanocrystals, we applied a novel molecular doping concept into tuning the electronic structure of NiO HTLs by TCNQ molecule series. The electron transfer from NiO nanocrystals to the F6TCNNQ molecules absorbed at their surface was observed and verified for the first time by electrostatic force microscopy and the first principle calculations, respectively. The band level offset at the interface of perovskite/NiO shrank from 0.18 to 0.04 eV, which boosted the conversion efficiency of the CxFAMA mixed cations PSCs approaching 21%. Surface molecular doping can not only applied successfully to NiO, but also SnO2, which is also a promising component to planar PSCs. That will be also discussed in this presentation. This methodology definitely paves a novel way to modulate the doping in hybrid electronics more than perovskite and organic solar cells.

4:15 PM ET05.14.10
Effect of the Interfacial Energy Between Perovskite and Precursor Solution on the Crystallization of Hybrid Organic-Inorganic Perovskites
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Hybrid organic-inorganic perovskite thin films or crystals are usually prepared from the precursor solution. The crystallization of perovskite is affected by the supersaturation of the perovskite precursors in solution and the interfacial energy between the perovskite and solvent. Here, I will present some of our methods to prepare high-quality perovskite thin films and crystals by varying the interfacial energy between perovskite and solvent. The high-quality perovskite thin films lead to highly efficient perovskite solar cells.

4:30 PM ET05.14.11
Quantification of Self-Illumination in >90% Internal Photoluminescence Quantum Efficiency Hybrid Perovskites
Roberto Brener1, Madeleine R. Laitz2,1, Dane W. deQuilettes1, Joel Jean1, Zahra Andaji-Garmaroudi2, Samuel D. Stranks1,2 and Vladimir Bulovic2; 1RL, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Photon recycling is critical for achieving record-high open-circuit voltages (Voc) and power conversion efficiencies (PCE) in single-junction GaAs solar cells. This phenomenon can be observed only in materials with extraordinarily high photoluminescence quantum efficiency (PLQE) and small escape cones. Photon recycling has been observed in perovskite solar cells but has not significantly improved device performance thus far. With recent advances in perovskite material quality, photon recycling could produce practical gains in Voc and PCE. However, the achievable gains in today’s materials remain uncertain. Here we investigate photon recycling in the most emissive (>90% internal PLQE) perovskite films reported to date—humidity-passivated CH3NH3PbI3, phosphine-oxide-passivated CH3NH3PbI3, and KI-passivated triple-cation perovskites (Cs0.06FA0.79MA0.15Pb(I0.85Br0.15)3). We use photoemission, X-ray absorption, and transient optical spectroscopy to probe the energy level alignment and exchange of charge carriers between the perovskite and adjacent Pt back contact. Using experimentally measured rate constants and material parameters, we develop a rigorous framework for quantifying (the extent of) photon recycling in thin-film samples and predicting the associated Voc and PCE gains. This analysis clarifies the opportunity for photon recycling to push the real-world performance of perovskite solar cells toward theoretical limits.

4:45 PM ET05.14.12
What Can be Learned From Self-Healing in Halide Perovskites?
Davide R. Cerati1, Yevgeny Rakita1, Llorenc Cremonesi2, Ron Tenne2, Vyacheslav

[1] Philip Schulz, IPVF, Centre National de la Recherche Scientifique, Palaiseau, France.
Among the aspects of Halide Perovskites, HaPs, which make them such fascinating materials the different time-scales of the dynamics of interconnected processes stand out. Short-time behavior (< sec) is determined by electronic charge carrier dynamics, while longer time effects are typically due to atom/ion dynamics, characteristic of halide perovskites, such as ion/defect movement, self-healing and others [1-3]. These slower processes are likely interdependent and hitherto not (well) elucidated, both as phenomena per se, and in terms of effects on the performance of HaP-based devices. Our recent work [2] provides clear evidence for self-healing, i.e., under certain conditions damage in optical properties can be reversed and, in particular, the status quo ante [3] can be re-established completely or mostly, in several types of Br-based HaP single crystals, as measured by 2-photon confocal microscopy. We demonstrated qualitatively but unequivocally that the effect is an intrinsic property of the materials, as it was measured in the bulk of single crystals, with typical times of minutes to hours.

Here we report on the products of decomposition and possible chemical pathways that can lead to self-healing, paying particular attention to the kinetics of the phenomena. We include now quantitative results of our experiments following the degradation/healing process kinetics in situ and of the energy-dependent damage threshold. We also show results for the more intensely studied Methylammonium, MA-, and Formamidinium, FA-PbI3.

Furthermore, we measure, analyze and explain the crucial differences between the light-induced damaging and recovery mechanisms in the bulk and at the surface under different atmospheres (i.e. air, N2, Br2, I2).

Finally, we measure and analyze the temperature dependence of the healing process, as it provides information about the energy of formation of the material from their binary halide constituents. This follows and compares to the reported positive enthalpy of formation of the Br and I MAPb perovskites [4-5], viz. their entropic stabilization.

We will put our results in the broader perspective of other HaP physico-chemical properties and performances of HaP-based device characteristics.

References