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 polarization 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.

Halide Perovskites—One of a Kind or Harbinger of Novel Optoelectronic Materials

9:30 AM *ET05.01.03

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

Mathias Meyers1, David A. Egger1, Andrew M. Rappe1 and David Reichman2; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Chemistry, Columbia University, New York, New York, United States; 3University 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 transitions 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) possess (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 cm2V-1s-1) with those of other semiconductors, such as GaAs or CdTe (~103-105 cm2V-1s-1), 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), support the characterization of methylammonium as a lattice polar liquid within the CH3NH3PbBr3 crystal. The Br 3d5/2 core level Debye-Waller factor plots exhibited a temperature dependence indicative of an effective Debye temperature of 160±61K, while the Pb 4f7/2 core-level Debye-Waller factor plots exhibited a temperature dependence indicative of an effective Debye temperature of 160±61K, while the Pb 4f7/2 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$^1$, Kai Xiao$^2$, Benjamin Doughty$^3$, Yingzhong Ma$^4$ and Joshua Choi$^5$; $^1$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 $(\mu+t)^{\eta}$, where $\mu$ and $\eta$ are the octahedral factor and the atomic packing fraction respectively. As a stability descriptor $(\mu+t)^{\eta}$ 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 $(\mu+t)^{\eta}$ 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,
Further breakthroughs in perovskite solar cells require advances in new compositions and underpinning materials science. Indeed, a greater fundamental understanding of perovskite materials requires atomic-scale characterization of their underlying structural, defect and transport behaviour. In this context, combined modelling-experimental work is now a powerful approach for investigating these properties at the atomistic level. This presentation will describe such studies on hybrid perovskites [1-3] in two related areas: (i) the defect and ion transport properties of methylammonium lead iodide (MAPbI3) in relation to atmospheric effects and degradation; (ii) the molecular cation dynamics and octahedral distortion of halide perovskites with mixed A-cations (MA, FA, CA) in relation to their improved stability and photovoltaic performance.


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

2:45 PM ET05.02.04
Huge Enhancement of Ion Conduction and Implications for Photo-Deposition in Hybrid Organic-Inorganic Lead Halides Perovskite
Gee Yeong Kim1, Alessandro Senocrate1, Tae-Youl Yang2, Giuliano Gregori2, Michael Graetzel2 and Joachim Maier1; 1Max Planck Institute for Solid State Research, Stuttgart, Germany; 2Swiss Federal Institute of Technology in Lausanne, Lausanne, Switzerland.

Methylammonium lead iodide (MAPI) is the archetype material of the class of halide perovskites that are currently in the focus of photovoltaic research because of high conversion efficiencies. MAPI exhibits some anomalies properties such as a huge apparent low frequency dielectric constant and severe hysteretic current-voltage behavior. In order to investigate the key features of its performance, not only electronic, but also ionic transport properties need to be considered [1,2]. Here we report on huge photo effects on ion conductivity in MAPI. To measure and separate both transport contributions not only in the dark, but also under illumination, we carried out a variety of tailored electrochemical studies. In this way, an enhancement of ionic conductivity by as much as two orders of magnitude in MAPI by light illumination can be unambiguously demonstrated [3]. The mechanism of ion conduction under light is proposed to rely on a translation of a great fraction of the generated holes into iodine vacancies which are the ionic charge carriers. Localized holes correspond to neutral iodine which can -owing to site and poly-anionic stabilization- occupy interstitial sites leaving vacant iodine sites that are causing the ionic conductivity. This process is reversible under homogeneous conditions. If, however, iodine is irreversibly removed under illumination, photo-decomposition occurs. This unexpected finding does not only give rise to a decomposition path for metal halide perovskites, it also allows one to tune ion transport by light.

References

3:00 PM BREAK

3:30 PM *ET05.02.05
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 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.

4:00 PM ET05.02.06
Quantification of Ion Migration in Halide Perovskites with Potassium Passivation
Moritz H. Futschel1, 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 Kim3, Igor Moudrakovski1, Tae-Youl Yang1, Giuliano Gregori1, Michael Gratzel1 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 perovskite 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] 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] 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 Binwe Subedi, Chongwen Li, Cong Chen, Maxwell Junda, Dewei Zhao, Yanta Yan and Nikolaj Podzurik; 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 FASn0.6Pb0.4I1-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 FASn0.6I0.4Pb0.4Br0.6 (x ≤ 0.15) show materials prepared with x ≤ 0.04 having the lower Urbach energy than higher Br content. In FASn0.6PbI3, 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.
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 electron 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 interfacial layer and the perovskite film.

performance of light-emitting diode (LED), and other optoelectronic devices. Until now, ligand exchange, reducing ligand chain and ligand density control are adopted to increase 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 methylenamine lead bromide (MAPbBr3) QDs with an unsaturated conjugated alkyl-amine, 3-Phenyl-2-propen-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.

**ET05.03.05**

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

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

Multicomponent quasi-two-dimensional perovskites (Q-2DPs) 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 Q-2DPs, leading to large photovoltage loss in PSC. Therefore, we develop a p-i-n bulk heterojunction (BHJ) structure to reduce the nonradiative recombination. We obtain high \(V_{oc}\) of 1.18 V for (PMA)\(\text{MA}\)\(\text{Pb}_{1.5}\)\(\text{Cl}(N=5)\) in PSC, much higher than the planar counterparts. The enhanced efficiency is attributed to the improved exciton dissociation via BHJ interface. Our results provide an important step towards high \(V_{oc}\), and stable 2D PSCs, which could be used for tandem solar cell and color photovoltaic windows.

**ET05.03.06**

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

Lingling Mao, Weijun Ke, Laurent Pedesseau, Claudine Katari, Jacky Even, Constantinos Stoumpos and Mercour G. Kanatzidis; Chemistry, Northwestern University, Evanston, Illinois, United States; Univ 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)piperidinium (3AMP) or 4-(aminomethyl)piperidinium (4AMP) as spacing cations. The general formula for the DJ perovskite is \(A^2A_3\), \(\text{Pb}_{1.5}\) (3AMP or 4AMP, \(A = \text{methylammonium (MA)}\). Compared with the Riddlesden–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, where the (3AMP)(MA)(\(\text{Pb}_{1.5}\) has the best PCE of 7.3%, much higher than the corresponding (4AMP)(MA)(\(\text{Pb}_{1.5}\)). With compositional engineering on the existing system, we optimize the device performance of (3AMP)(MA)(\(\text{Pb}_{1.5}\)) (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 \(\text{CH}_3\text{NH}_2\text{Pb}_x\) \((x = 1, Cl, I)\) (Science, 356, 1376 (2017)), inorganic perovskite \(\text{CsPbX}_3\) 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 CsPbX3 or CsSnX3) 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 unannealed \(\text{CsPbBr}_3\) thin films fabricated by thermal evaporation exhibit ultralow ASE threshold of \(3.3 \mu\text{J/cm}^2\), 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 \(\text{CsPbBr}_3\) 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 \(\text{CsPbBr}_3\) thin films as practical optical gain media for further light-emitting applications.

**ET05.03.08**

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

Eric W. Welch, Amanda J. Neukirch, Sergei Tretiak, Petr Obraztsov, Dmitry Lyashenko, Pavel Chizhov, Kuniaki Konishi, Natsumi Nemoto, Makoto Kuwata-Gonokami, Petr Obraztsov and Alex Zakhidov; Texas, United States; Univ Rennes, Rennes, France.

Multicomponent quasi-two-dimensional perovskites (Q-2DPs) 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 Q-2DPs, leading to large photovoltage loss in PSC. Therefore, we develop a p-i-n bulk heterojunction (BHJ) structure to reduce the nonradiative recombination. We obtain high \(V_{oc}\) of 1.18 V for (PMA)\(\text{MA}\)\(\text{Pb}_{1.5}\)\(\text{Cl}(N=5)\) in PSC, much higher than the planar counterparts. The enhanced efficiency is attributed to the improved exciton dissociation via BHJ interface. Our results provide an important step towards high \(V_{oc}\), and stable 2D PSCs, which could be used for tandem solar cell and color photovoltaic windows.
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 Organo-Metal Halide Perovskite Quantum Dots via Surface Energy Manipulation  
Som Sarang1, Sara Bonabi2, Parveen Kumar3, Michael Scheibner1, Vincent Tung1, Jin Zhang1 and Sayantani Ghosh1; 1University of California, Merced, Merced, California, United States; 2University of California Santa Cruz, Santa Cruz, California, United States.

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 CH3NH3PbI3 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, homoepitaxy, and low challenge 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, homoepitaxy, and low

ET05.03.11  
High Stability and Ultralow Threshold Amplified Spontaneous Emission from Formamidinium Lead Halide Perovskite Films  
Xiaoyun Liu, Xi’an Jiaotong University, Xi’an, China.

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(NH3)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 efficient excitation 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 continuous wave pumped lasers and electrically driven lasers.

ET05.03.12  
A Novel Series of Quasi-2D Ruddlesden-Popper Perovskites Based on Short-Chain Spacer Cation for Enhanced Photodetection  
Dong Ruoting, Changyong Lan, Xiwen Xu and Johnny Ho; City University of Hong Kong, Hong Kong, Hong Kong.

Quasi two-dimensional (2D) layered organic-inorganic perovskite materials (e.g. (BA)2(AM)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(AM)n−1PbnI3n+1 perovskites, where the relatively pure phase (iBA)2PbI4 and (iBA)2MA3Pb4I13 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(AM)n−1PbnI3n+1 perovskites exhibit much enhanced photodetection properties without sacrificing their excellent stability. Through hot-casting, the optimized (iBA)2(AM)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 figures-of-merit 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  
Celine A. Omondi1, Katrin

Celline A. Omondi1, Katrin

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, $E_g$, $E_T$ and $L$ are not necessarily constant and can depend, for example, on the preparation conditions and degradation. Therefore, $E_g$, $E_T$ 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 $E_g$, 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$_3$. The $E_g$ of CH$_3$NH$_3$PbI$_3$ 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 $E_g$ and of CH$_3$NH$_3$PbI$_3$ films was investigated. It has been found, for example, that $E_g$ and 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 showed a constant band gap of 1.58 eV and a low scatter in $E_g$. This was attributed to the modification of the TiO$_2$/PCBM 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 $E_g$ 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*  
Tanghao Liu$^{1,2}$, Yuanyuan Zhou$^1$, Nitin Padture$^1$, Kai Zhu$^1$, Rui Zhu$^2$ and Deying Luo$^2$; $^1$Brown University, Providence, Rhode Island, United States; $^2$School of Physics, Peking University, Beijing, China; $^3$National Renewable Energy Laboratory, Golden, Colorado, United States.

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 solar 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, SiO$_2$ passivates defects and reduces the recombination, enhancing the photovoltaic performance. Using the in situ grain encapsulation strategy, FA-based PSCs can exhibit a power conversion efficiency of 19.5% and keep stable for 1000 h in the ambient atmosphere.

**ET05.03.15**

*Modification of Excitonic Properties of Halide and Mix-Halide Hybrid Perovskite Thin Films Using Interface Engineering*  
Katerina Nikolaidou$^1$, Som Sarangi$^1$, Denzal Martin$^1$, Vincent Tung$^1$, Jennifer Liu$^1$ and Sayantani Ghosh$^1$; $^1$Physics, University of California, Merced, Merced, California, United States; $^2$Materials Science and Engineering, University of California, Merced, Merced, California, United States.

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$_3$) halide hybrid perovskite thin films. The perovskite/ZnO interfaces are characterized by means of electron microscopy correlated with charge transfer properties that are probed by temperature, power and 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$_3$Bi$_2$I$_6$Cl$_3$ (A = Cs, Rb)—Exploring the Limits of the Defect Perovskite Structure*  
Kyle M. McCall, Grant C. Alexander, Oleg Kontsevoi, Bruce Wessels and Mercouri G. Kanatzidis; Northwestern University, Evanston, Illinois, United States.

Halide perovskites have remarkable optoelectronic 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$_2$)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$_3$ octahedral framework with trivalent M$^{3+}$ are the defect perovskites A$_3$M$_3$X$_6$. We have been investigating the optoelectronic properties of the iodide defect perovskites A$_3$M$_3$X$_6$ (A = Cs, Rb; M = Sb, Bi), finding that these four compounds have strong electron-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$_3$X$_6$ are not entirely isosstructural. 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$_3$Bi$_2$I$_6$ has a 0D dimer structure of isolated Bi$_2$I$_6$ octahedra, while Cs$_3$Sb$_2$I$_6$ can form either of these structures depending on preparation method. Even the 2D Rb$_3$Sb$_2$I$_6$ 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$_3$Bi$_2$I$_6$, resulting in the novel 2D defect perovskite
In the colloidal synthesis of inorganic perovskite materials, cesium oleate (CsOL) is the most commonly used Cs precursor. This precursor is synthesized by combining oleic acid with either cesium carbonate (Cs₂CO₃) or cesium acetate (CsOAc), and the long alkyl chain of CsOL is expected to impart solubility in the non-polar solvents used in synthesis, similar to Pb(oleate). However, despite its ubiquitous use in literature, CsOL has been observed to be insoluble at room temperature and leads to surprisingly inconsistent results in perovskite nanocrystal synthesis depending on the Cs salt from which the precursor is derived. We show that under the conditions used in most reports, the amount of oleic acid (OA) added, while stoichiometrically sufficient, still leads to incomplete conversion of the Cs salts to CsOL. This results in a mixture of Cs sources being present during the reaction, causing decreased homogeneity and reproducibility. When a proper Cs/OA ratio is used, complete conversion is readily obtained even under mild conditions, resulting in a precursor solution that is soluble at room temperature and yields identical synthetic results regardless of the initial Cs source. Further, ¹H NMR of solutions prepared using varying Cs/OA ratios confirms that the maximum ratio of Cs:OA obtainable in solution, with any excess Cs present in the precipitate. The super-stoichiometric ratio observed is attributed to the monovalent nature of the Cs cation which leads to a permanent dipole moment in Cs oleate, reducing solubility compared to commonly used divalent oleate complexes such as Pb(oleate). Dynamic light scattering reveals that the addition of Cs yields a reverse micelle-like structure with a diameter of 3.1 nm, consistent with the excess oleic acid complexing with the CsOL in the nonpolar solvent. Careful control of the ligand ratio yields a fully soluble precursor, which is shown to enable facile, reproducible, and scalable synthesis via the slow addition of precursors, with the notable ability to control morphology through injection rate.

Inorganic perovskite materials, cesium oleate (CsOL) is the most commonly used Cs precursor. This precursor is synthesized by combining oleic acid with either cesium carbonate (Cs₂CO₃) or cesium acetate (CsOAc), and the long alkyl chain of CsOL is expected to impart solubility in the non-polar solvents used in synthesis, similar to Pb(oleate). However, despite its ubiquitous use in literature, CsOL has been observed to be insoluble at room temperature and leads to surprisingly inconsistent results in perovskite nanocrystal synthesis depending on the Cs salt from which the precursor is derived. We show that under the conditions used in most reports, the amount of oleic acid (OA) added, while stoichiometrically sufficient, still leads to incomplete conversion of the Cs salts to CsOL. This results in a mixture of Cs sources being present during the reaction, causing decreased homogeneity and reproducibility. When a proper Cs/OA ratio is used, complete conversion is readily obtained even under mild conditions, resulting in a precursor solution that is soluble at room temperature and yields identical synthetic results regardless of the initial Cs source. Further, ¹H NMR of solutions prepared using varying Cs/OA ratios confirms that the maximum ratio of Cs:OA obtainable in solution, with any excess Cs present in the precipitate. The super-stoichiometric ratio observed is attributed to the monovalent nature of the Cs cation which leads to a permanent dipole moment in Cs oleate, reducing solubility compared to commonly used divalent oleate complexes such as Pb(oleate). Dynamic light scattering reveals that the addition of Cs yields a reverse micelle-like structure with a diameter of 3.1 nm, consistent with the excess oleic acid complexing with the CsOL in the nonpolar solvent. Careful control of the ligand ratio yields a fully soluble precursor, which is shown to enable facile, reproducible, and scalable synthesis via the slow addition of precursors, with the notable ability to control morphology through injection rate.

Hybrid organic-inorganic metal perovskites (chemical formula: ABX₃, A-organic cation, B-metal ion, X-halide) are the latest advancement for increasing efficiency in thin-film solar cells or Dye solar cells (DSC). They have become the fastest growing technology in solar cells, rising in efficiency from 3% to 20% in less than a decade. This work focuses on a time-dependent density-functional theory (TDDFT) study of CH₃NH₃PbCl₃ - methylammonium lead chloride - a perovskite material of potential and current research interest. Both the cubic and tetragonal phases are investigated. The cubic phase for CH₃NH₃PbCl₃ is the room temperature phase for this configuration of the perovskite and it crystallizes in the Pnm3m space group, while the tetragonal phase crystallizes in P4/mmm space group. The cubic structure has an outer PbCl₃ octahedra and a central organic methylammonium cation (CH₃NH₃⁺). Each Pb is bonded to three Cl atoms, and the ionic structure is derived. We show that under the conditions used in most reports, the amount of oleic acid (OA) added, while stoichiometrically sufficient, still leads to incomplete conversion of the Cs salts to CsOL. This results in a mixture of Cs sources being present during the reaction, causing decreased homogeneity and reproducibility. When a proper Cs/OA ratio is used, complete conversion is readily obtained even under mild conditions, resulting in a precursor solution that is soluble at room temperature and yields identical synthetic results regardless of the initial Cs source. Further, ¹H NMR of solutions prepared using varying Cs/OA ratios confirms that the maximum ratio of Cs:OA obtainable in solution, with any excess Cs present in the precipitate. The super-stoichiometric ratio observed is attributed to the monovalent nature of the Cs cation which leads to a permanent dipole moment in Cs oleate, reducing solubility compared to commonly used divalent oleate complexes such as Pb(oleate). Dynamic light scattering reveals that the addition of Cs yields a reverse micelle-like structure with a diameter of 3.1 nm, consistent with the excess oleic acid complexing with the CsOL in the nonpolar solvent. Careful control of the ligand ratio yields a fully soluble precursor, which is shown to enable facile, reproducible, and scalable synthesis via the slow addition of precursors, with the notable ability to control morphology through injection rate.

Achieving Full Solubility—The Hidden Role of Oleic Acid in Cs Oleate Precursor Preparation for Perovskite Synthesis Chane Lai, Marcus Wright, Xiao Ma, Hui Li, Dominique S. Ibanez, Corey Hewitt, David L. Carroll and Scott M. Geyer; Wake Forest University, Winston Salem, North Carolina, United States.

In organic perovskite solar cells, achieving high photoluminescence quantum yield (PLQY) of OHPs film is critical to hinder the efficiency improvement of OHP film based light-emitting diodes. However, for light-emitting applications, the low photoluminescence quantum yield (PLQY) of OHPs film is critical to hinder the efficiency improvement of OLED 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 insulating 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 PLQY. It is reported that Cs introduction to perovskite leads to improved PLQY and better stability of device, for example, device efficiency increased form 2.76cd/A to 10.09cd/A. While CsBr exhibits low solubility in solvent which leads to the difficulty in preparation for Cs-doping provskite film, 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 65535cd/m², EQE of 7.17% and a highest efficiency of 24.22cd/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 Rb ion replaces the site of FA+ partially, and distorts the crystal structure of FAPbBr₃, thus affects the photoelectronic 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.
Two-Dimensional (2D) Halide Perovskites Incorporating Straight Chain Alkylidiammonium Cations, \((\text{NH}_3\text{C}_m\text{H}_{2m}\text{NH}_3)(\text{CH}_3\text{NH}_3)^{n-1}\text{Pb}_n\text{I}_{3n+1}, m = 4-9 \ n = 1-4\) Xiaotong Li, Jean-Claude Marder, Justin Hoffman, Jin-Seok Lee, Michelle Chen, Hisanori Tsai, Mikhail Kepenekian, Kostas Kanatzidis; 1Department of Chemistry, Northwestern University, Evanston, Illinois, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3Institut des Sciences Chimiques de Rennes, Rennes, France.

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 (\(\text{NH}_3\text{C}_m\text{H}_{2m}\text{NH}_3)(\text{CH}_3\text{NH}_3)^{n-1}\text{Pb}_n\text{I}_{3n+1}, m = 4-9 \ n = 1-4\)) where \(m\) represents the carbon-chain number and \(n\) equals layer-thickness number. Multilayer (\(n > 1\)) 2D perovskites incorporating diaminocyanide cations were successfully synthesized by solid state grinding method for \(n = 4\) and \(6\), and by solution method for \(m = 7\). 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 \(C_c\) for even \(n\) members and \(P_c\) 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 \((\text{NH}_3\text{C}_m\text{H}_{2m}\text{NH}_3)(\text{CH}_3\text{NH}_3)^{n-1}\text{Pb}_n\text{I}_{3n+1}\) 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 energies, which results in low luminous efficiencies. One of the proposed strategies to enhance the exciton binding energy is to reduce the dimensionality of the perovskite crystal structure. Here, we report high 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 FA\textsubscript{2}Pb\textsubscript{3}Br\textsubscript{9} and a new type of 2D perovskite FA\textsubscript{2}PbBr\textsubscript{6} intercalated with dimethyl sulfoxide (DMSO) was formed by controlling the molar ratio of FA\textsubscript{2}PbBr\textsubscript{6} in the precursor solutions and annealing condition. A type I band alignment between the lower bandgap 3D FA\textsubscript{2}PbBr\textsubscript{6} and the higher bandgap 2D FA\textsubscript{2}PbBr\textsubscript{6} was supported by density functional theory (DFT) calculations, which results in exciton 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**

Hisato Yamauchi, Fangze Liu, Hsinhan Tsai, Michael D. Yoho, Aditya D. Mohite, Sergei Tretiak, Duc T. Vo and Wanyi Nie; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

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 (MAPbBr\textsubscript{3}) 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 \( \mu \)m. 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 further 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 caesium lead bromide (CsPbBr\textsubscript{3}) 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 PbBr\textsubscript{2}, we investigate the electronic structure and their contribution to the overall electronic structure of our CsPbBr\textsubscript{3}. Films prepared with varying concentrations of the precursor materials up to the full perovskite structures 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 (HOIHPs) 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, HOIHPs are known to easily degrade under moderate thermal stress\textsuperscript{1} or upon oxygen\textsuperscript{2} and/or light exposure\textsuperscript{3}. Notably, recent calorimetric studies even suggested that some HOIHPs (MAPb\textsubscript{x}I\textsubscript{1-x} in particular and MAPbBr\textsubscript{2} to a minor extent) could be thermodynamically unstable\textsuperscript{4} in agreement with DFT calculations.\textsuperscript{5} In contrast, other studies indicate the materials to be intrinsically stable.\textsuperscript{6} Obviously these questions need to be unambiguously answered. In this contribution, we discuss the underlying thermodynamics of HOIHPs, 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 MAPbI\textsubscript{x}I\textsubscript{1-x}, 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 HOIHPs in the presence of oxygen, especially under real conditions. Notably, light itself can activate a relevant photodecomposition pathway.\textsuperscript{7} We discuss these issues on a quantitative level, in conjunction with experimental observations of the degradation phenomena.

References

Enhanced Photoreponse in Hybrid Perovskite Thin Film via Integrating with MoS2

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Over the past five years, the organolead trilhalide 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 photoreponse 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 photoreponse of 200-300 µs, which makes it promising for constructing high performance photo-detectors.

Enhanced Photoreponse in Hybrid Perovskite Thin Film via Integrating with MoS2
based tunable band gap makes these systems ideal candidates for multi-junction solar cells. Unfortunately, there has been relatively little work done to explore perovskite 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,MA1-xPbI(x) films using a spatially-resolved, super-resolution hot-electron photothermal heterodyne imaging (HR-PHII) 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 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 photovoltaic 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

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Interfacial studies and band 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 SnO2(a-SnO2) between the TiO2 ETL and the perovskite absorber and studied on the charge transport properties of the device. The double-layer structure of TiO2 compact layer (c-TiO2) and a-SnO2 ETL leads to modification of interface energetics, resulting in improved charge collection and decreased carrier recombination in PSCs. The optimized device based on a-SnO2/c-TiO2 ETL shows a maximum power conversion efficiency (PCE) of 21.4% as compared to 19.33% for c-TiO2 based device. Moreover, the modified device demonstrates a maximum open circuit voltage (Voc) 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-TiO2/a-SnO2 retains about 91% of its initial PCE value after 500 h light illumination, which is higher than pure c-TiO2 (67%) based devices. Interestingly, using a-SnO2/c-TiO2 ETL the PCE loss was only 10% of initial value under continuous UV light illumination after 30 h, which is higher than that of c-TiO2 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., Cs4CuSb2Cl12-like Cs4M2+B3+2XVII12 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, high hole effective masses and intrinsic good p-type conductivity, respectively. Taking CsCdSbCl12 as a representative example, we demonstrate that under Cd-poor (Cl-rich) conditions, CsCdSbCl12 could exhibit excellent p-type conductivity with high hole concentration, contributed by the intrinsic shallow-acceptor Cd9, with extremely low formation energy. Generally, the other 6 Cs4M2+B3+2XVII12 compounds exhibit similar intrinsic p-type defect properties as CsCdSbCl12, 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 Rehermann3, Eva L. Unger2, Gary Hodes1, Isaac Balberg3, David Cahen1 and Thomas Dittrich2; 1Weizmann Inst of Science, Rehovot, Israel; 2Solar, Pandit Deendayal Petroleum University, Gujarat, India; 3Sharif University of Technology, Tehran, Iran (the Islamic Republic of).

Lead Bromide-based perovskites (HPs) 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 photovoltaic performance, especially in the open circuit voltage (Voc) of the cell.

However, since several studies showed that the concentration of defects in the HPs is relatively low (~ 1016 cm-3), there is a general difficulty to observe deep in-gap states by direct optical absorption of sub-band gap photons in the HPs. 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 directivity for the HP materials.

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 band edges, 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 (PLQE). The corresponding LEDs exhibit stable spectral emission and good performances (e.g., irradiance of 400 W/m2...
Effect of Chromium Doping on the Electronic Structure of CH$_3$NH$_3$PbI$_3$ Perovskite

ET05.03.38

Highly Luminescent 0D Organic Metal Halide Hybrids with Tunable Colors Chenkun Zhou$^{1}$, Haoran Lin$^{1}$, Michael Worku$^{1}$, Jennifer Neuf$^{1}$, Yan Zhou$^{1}$, Yu Tian$^{1}$, Peter I. Djurovich$^{2}$, Theo Siegrist$^{3}$ and Biwu Ma$^{4}$; $^{1}$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 electronic properties of these functional materials 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 and provide a general overview of the non-inorganic inorganic metal halide hybrids.

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$^{1}$ 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 casting, 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 morphology 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 vacuities 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 3-5 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 Perla Wahnon-Benarroch$^{1}$, Gregorio Garcia$^{1}$, Pablo Palacios$^{1}$, Jose Carlos Conesa$^{2}$, Ana Lilian Montero$^{2}$ and Eduardo Menendez-Proupin$^{2}$; $^{1}$Univ Politecnica de Madrid, Madrid, Spain; $^{2}$Consejo Superior Investigaciones Cientificas, 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, CuGaS$_2$, thiopyrins, SnS$_2$ or Si. We report here the electron structure of new CH$_3$NH$_3$PbI$_3$ perovskite derivatives, in which narrow band is obtained by replacing Pb atoms by Cr atoms. To deal with the bandgap underestimation problem of common DFT methods, quasiparticle calculations have been applied via the GW approximation. The investigation of the electronic structure of new CH$_3$NH$_3$PbI$_3$ perovskites suggests that the presence of point defects play an important role in the coupling of two low energy photons to achieve a higher energy electron excitation (like in the Z-scheme of photosynthesis), which would maximize the photovoltaic performance.

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 McCluskey$^{1}$, David Stewart$^{1}$, Tod Grusenmeyer$^{1}$, Thomas M. Cooper$^{1}$ and Joy Haley$^{1}$; $^{1}$Air Force Research Laboratory, Dayton, Ohio, United States; $^{2}$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, Seattle, United States.

We measure the inter-diffusion of methylammonium (MA) and formamidinium (FA) cations using lateral heterojunctions formed between MAPbI$_3$ and FAPbI$_3$. 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 MAPbI$_3$ portion and ~1.49 eV for the FAPbI$_3$ 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$^2$s$^{-1}$. 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 MAPbI$_3$ to FAPbI$_3$. 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.

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**SESSION ET05.04: Photophysics, Carrier Dynamics and Device Mechanisms**

**8:00 AM ET05.04.01**

**Are Charge-Carrier Recombination Processes in Halide Perovskites Unique?**

Dane W. deQuilettes$^{1,2}$, Kyle Frohna$^1$, David Emiri$^3$, Thomas Kirchartz$^4$ and Samuel D. Stranks$^1$; $^1$Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; $^2$Chemistry, University of Washington, Seattle, Washington, United States; $^3$University of Cambridge, Cambridge, United Kingdom; $^4$The University of New Mexico, Albuquerque, New Mexico, United States; $^5$Universität 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 Sridharan$^1$, Nakita K. Noel$^2$, Hyeon Hwang$^3$, Sorosh Hafezian$^1$, Barry P. Rand$^2$ and Stéphane Kéna-Cohen$^1$; $^1$Engineering Physics, Polytechnique Montréal, Montreal, Quebec, Canada; $^2$Electrical 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 MAPbI$_3$, obtained via different fabrication routes, FAPbI$_3$, FA$_0.85$MA$_{0.15}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ and MAPbBr$_3$. Small diffusion coefficients of ~0.9 × 10$^{-5}$ and ~2.1 × 10$^{-5}$ cm$^2$s$^{-1}$ are found in the films showing the highest device efficiencies, i.e., in FA$_{0.85}$MA$_{0.15}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ and MAPbI$_3$ (acetonitrile processed), respectively. In contrast, much higher values are found in MAPbI$_3$ and FAPbI$_3$ films, i.e. 4.9 × 10$^{-3}$ cm$^2$s$^{-1}$ and 2.7 × 10$^{-3}$ cm$^2$s$^{-1}$, respectively. We find that in addition to diffusion, the interplay between the monomolecular and bimolecular recombination processes is a critical factor determining device efficiency.
interaction of carriers with optical vibrations of the lead halide lattice (Fröhlich interaction)\(^2\). Therefore, predictions of maximum attainable mobilities can be made from easily accessible parameters, such as LO phonon frequencies and limits of the dielectric function.\(^3\)

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,\(^3\) and exhibit a dynamic that is heavily influenced 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 opened circuit voltages.


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 Wall; 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 archetypal hybrid perovskite, CH\(_3\)NH\(_3\)PbI\(_3\). 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 PEA\(_2\)PbI\(_4\)(MAPbI\(_3\))\(_{0.7}\) (PEA, phenylethylammonium; 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 rates 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 measured 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 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. 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. 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. 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.

References
\[1\] Ye Yang, Mengjin Yang, David T. Moore, Yong Yan, Elisa M. Miller, Kai Zhu and Matthew C. Beard, Nature Energy 2017, 2, 16207.

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.
A major puzzle from recent studies on LHPs is that optoelectronic performances suggest nearly perfect semiconductors despite the unavoidable presence of defects from high temperature and solution processing. Here we explain the essential physics in this class of materials based on their distinct phonon dynamics and dielectric functions. We show that the dielectric function of a hybrid organic-inorganic lead halide perovskite (LHP) possesses combined characteristics of a polar liquid and a ferroelectric material. The latter response in the THz region may lead to dynamic and local ordering of polar nano domains by an extra electron or hole, resulting a quasiparticle which we call a ferroelectric large polaron. Compared to a conventional large polaron, the collective nature of polarization in a ferroelectric large polaron may give rise to order(s)-of-magnitude larger reduction in the Coulomb potential and introduce potential barriers to charge carrier scattering. The ferroelectric large polaron may explain the defect tolerance, low recombination rates, and slow cooling of charge carriers in lead halide perovskites, as well as providing a design principle for high performance semiconductors from nano, molecular, and hybrid materials.

10:45 AM *ET05.04.08
Loss Mechanisms in Perovskite Solar Cells—Initially and During Aging Wolfgang Tress; LSPM, EPFL, Lausanne, Switzerland.

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 photovoltiac 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. 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. 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. 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

11:15 AM ET05.04.09
Imaging the Inhomogeneous Trap State Distribution in Hybrid Organic-Inorganic Perovskite Films Andrew J. Winchester1, Christopher Petoukhoff1, Mojtaba Abdi Jalebi2, Zahra Andaji-Garmaroudi2, Vivek Pareek3, E Laine Wong1, Julien Madeo1, Michael K. L. Man1, Samuel D. Stranks2 and Keshav Dani1; 1Okinawa Institute of Science and Technology, Okinawa, Japan; 2Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

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.

11:30 AM ET05.04.10
Recombination Routes of the Free Carriers in Perovskite Solar Cells Revealed by Intensity-Modulated Photovoltage Spectroscopy Xiaoqing Chen, Yasuhiro Shirai, Masatoshi Yanagida and Kenjiro Miyano; National Institute for Materials Science, Tsukuba, Japan.

In intensity-modulated photovoltage spectroscopy (IMVS) and impedance spectroscopy (IS) experiments of perovskite solar cells (PSCs), two features with different power dependences are observed: corresponding 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 two carrier species should be considered to explain the linear power dependence of the faster feature. Consequently, the next question is what this 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.
Origin of High Photoluminescence in Mixed-Cation Perovskites—Energetic Disorder Leads to Charge Localization

Sascha Feldmann1, Stuart MačpHERSON1, Jasmine Rivet1, Mojtaba Abdi Jalebi1, Satyapravad P. Senanayak1, Guangjun Nan2, David Beljonne2, Michael Saliba3, Samuel D. Stranks1 and Felix Deschler1; 1Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; 2Chimie des Matériaux Nouveaux, Université de Mons, Mons, Belgium; 3Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland.

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 dynamically 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.

11:45 AM ET05.04.11
Origin of High Photoluminescence in Mixed-Cation Perovskites—Energetic Disorder Leads to Charge Localization

Sascha Feldmann1, Stuart MačpHERSON1, Jasmine Rivet1, Mojtaba Abdi Jalebi1, Satyapravad P. Senanayak1, Guangjun Nan2, David Beljonne2, Michael Saliba3, Samuel D. Stranks1 and Felix Deschler1; 1Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; 2Chimie des Matériaux Nouveaux, Université de Mons, Mons, Belgium; 3Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland.

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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.


2:00 PM ET05.05.02/ET04.05.02
Photovoltaics of Halide Perovskites and Perspectives of Extensive Applications from the Ground to the Universe

Tsunomu 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 between −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

2:30 PM BREAK

3:00 PM ET05.05.03/ET04.05.03
Perovskite Photovoltaics—History, Progress and Perspective

Nam-Gyu Park; Sungkyunkwan University, Suwon, Korea (the Republic of).

Since the first report on the high efficiency, stable solid-state perovskite solar cell (PSC) in 2012 by our group, following two seed works on perovskite-
sensitized liquid junction solar cells in 2009 and 2011, PSC demonstrated its power conversion efficiency (PCE) of 22.7% in 2017. According to Web of Science, publications on PSC increase exponentially since 2012 and total number of publications reaches about 9,000 as of May, 2018, which is indicative of a paradigm shift in photovoltaics. Although high photovoltaic performance was achieved, current-voltage hysteresis has been issued because it is related to stability of PSC. In this talk, methodologies to remove hysteresis are described. Interlayers at heterojunction are found to play important role in reducing hysteresis and improving stability. Manipulation of Frenkel defect is a universal approach toward hysteresis-free PSC. We have discovered novel methods for large-area perovskite coating and phase transformation in perovskite, which will be discussed in detail. In addition to photovoltaics, perovskite can be used to other applications. Long charge diffusion length and high energy stability of organic-inorganic halide perovskite are suitable for low-dose, high-resolution X-ray imaging. We demonstrated X-ray image using millimeter thick perovskite film based on multicrystalline perovskite crystal with single-crystal-like optoelectronic properties. For heading toward Shockley–Queisser limit, research direction in PSC is proposed in this talk.

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/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 bandgap tunability through perovskite composition engineering can enable high-efficiency multijunction devices, including perovskite/perovskite, 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
dried at 120 °C for 1 h, and then dissolved at 150 °C under Ar. Next, a mixture of 1-octadecene and PbBr₂ was vacuum-dried at 120 °C for 1 h, and then mixed with Ar. Oleylamine and oleic acid were added to the solution. After complete dissolution of PbBr₂, the solution was heated to 180 °C. The solution of cesium oleate kept at 100 °C was injected into the PbBr₂ solution, and, 5 s later, the mixture was cooled in an ice-water bath. Synthesized CsPbBr₂ QD was precipitated by addition of tert-butyl alcohol, and then collected by centrifugation. After vacuum-drying for 1 day, yellow sample was obtained. For photobleaching test, the dried sample in a sample holder was placed on a plane light source of 468-nm blue LEDs with ~50 W m⁻² at room temperature; its absorption and PL spectra were measured at designated duration during and after 72-h irradiation using UV-vis and fluorescence spectrometers.

According to transmission electron microscopy, the obtained sample was cubic particles with an average size of 8 nm. CsPbBr₂, with cubic structure was verified from the X-ray diffraction pattern. A narrow PL peak was observed at ~520 nm under 468-nm excitation. During the continuous blue light irradiation, the sample color changed from yellow to black. Actually, its absorbance at 700 nm, in which CsPbBr₂ QD had no light absorption, increased as the irradiation duration prolonged. The PL intensity decreased to 20% of the initial intensity after 72-h irradiation, revealing photodegradation of CsPbBr₂ QD. During storage in the dark at room temperature after 72-h irradiation, body color of the degraded sample returned to yellow from black. This phenomenon was consistent with a change in absorption spectra. At the same time, recovery of PL intensity was observed. After storage for 18 days, the final PL intensity reached up to 90% of the initial intensity. Such recovery of degraded CsPbBr₂ QD gives us a hint to solve the photobleaching problem. In the presentation, the observed photobleaching and recovery will be discussed with further analyses.

**ET05.06.02**

**Understanding Grain Boundary Effects in Methylammonium Lead Bromide Films Using Electron Backscatter Diffraction (EBSD)**

Gede Adhyaksa¹, Sarah Brittain¹, Haralds Abolins², Andries Loó³, Xueying Li², Joel D. Keelor³, Yanqi Luo², Teodor Duevski¹, Ron M. Heeren³, Shane Ellis¹, David P. Fenning² and Erik Garnett¹; 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 misclassify 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**

**Investigation of A-Site Cations on Structural and Optoelectronic Properties of Pb-Sn and Pure Sn Double-Halide Perovskites**

Gabriella A. Tosado, Yi-Yu Lin and Qiuming Yu; University of Washington, Seattle, Washington, United States.

Hybrid organic-inorganic halide perovskites have emerged as a new family of optoelectronic materials because of their wide tunability in structural and optoelectronic properties via varying the compositions in A, B and X sites of the formula ABX₃. While the primary structural and optoelectronic properties of hybrid organic-inorganic halide perovskites are dominated by transient metal valent cations in the B-site and halide anions in the X-site, recent research has shown the impact of A-site monovalent cations on phase and device stability and the additional 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 AₓMₓ(Aₓ₋₁Mₓ₋₁)ₓ₋₁PbₓSnₓ(IₓBrₓ₋₁)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) and formamidinium (FA⁺, 2.53 Å) and GA⁺ (2.78 Å), the increase of 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⁺ increases 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 low band gap (1.26 eV) perovskite-Cs₀.₁₀(MA₀.₁₇FA₀.₈₃)₀.₉Pb₀.₂₅Sn₀.₇₅(I₀.₈₃Br₀.₁₇)₃. 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.

**ET05.06.04**

**Minimizing Non-Radiative Losses Through Rational Defect Passivation for High Performance Perovskite Light-Emitting Diodes**

Weidong Xu¹,² and Feng Gao²; ¹The Department 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 (EQEmax) of 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 Polarons at Methylammonium Lead Halide Perovskite Interfaces**

Mahshid Ahmadi¹, Maximilian Hieres¹, Emmanuel Mapes², Eric Lukos³, Juan Bisquert⁴, Joshua Sangoro⁴ 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[1-2]. 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 contribute in the overall carrier mobility unlike large polarons but they can form charge accumulations states[3]. Here, we conclude that ion migration and accumulation is not solely responsible for giant dielectric constant at low frequency in OMHPs but 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 performance 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 photo- and photovoltaics (IBPVs) [1,2], 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 [3,4] and compared with the energetics of dominant intrinsic defects, established as the vacancy defects VMA (dominant acceptor) and VBr (dominant donor) [4]. It is observed that depending on the chemical potential of relevant species, transition metals Zr, Hf, Nb and 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 IBPVs 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 [1]) and unfavourable (e.g. the Hoke effect [2]) 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 CH3NH3PbBr3I2-xI3 from X-ray diffraction, heat capacity measurements under illumination to quantify the nature of— and energy associated with light-induced disorder/disorder transitions.

References

ET05.06.09
Controlled Nucleation and Growth for Optimum Perovskite Film Morphology at Liquid-Electrolyte Interface—A Study by Electrochemical
Impedance Spectroscopy Priva Srivastava and Monojit Bag: Indian Institute of Technology Roorkee, Roorkee, India.

Perovskite Solar Cells (PSCs) have already attracted considerable attention attributed to its intriguing properties, showing a tremendous jump in efficiency from 3.8% by Kojima et al. (2009) to 22.1% 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 sometime 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 the Mott-Schottky plot for spin coated and spray coated films of methylammonium lead tri-iodide (MAPbI₃) perovskite. In this work, MAPbI₃ 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 (Tsubt) varied from room temperature to 120 °C prior to the coating. Nucleation and growth mechanism is revisited to find out the optimum Tsubt for fabricating uniform perovskite films and is attributed to the fast homogeneous nucleation followed by delayed growth. We confirmed that if the transformation temperature is just below the equilibrium melting point of the material, the nucleation is more homogeneous and hence more uniform and compact films are formed. EIS measurement at perovskite-liquid electrolyte interface reveals the impact of film morphology on the anomalous diffusion behaviour observed at low frequency regime and on the open circuit voltage (VOC) of the device. More uniform and compact films show less degree of diffusion across the interface as compare to the rough ones. Also the VOC (1.018 V) is highest for the device fabricated by more uniform and compact film (Tsubt = 100 °C) among all the devices followed by the one fabricated at Tsubt = 120 °C (0.963 V). This reveals that film morphology is an important factor in deciding the kinetics at the interface and VOC and hence the performance of the device.


ET05.06.10
Electrosprun Perovskite Fibers – New Flexible 1D Nanocomposites for Light Harvesting Applications Christinnae Behr1, Senol Oz, Ashish Lepcha1, Markus Schütz1, Florian Staub1, Thomas Fischer1, Thomas Kirchartz2 and Sanjay Mathur3; 1Institute of Inorganic Chemistry, University of Cologne, Cologne, Germany; 2IEK-5 Photovoltaik, Forschungszentrum Jülich GmbH, Jülich, Germany; 3Faculty of Engineering and CENIDE, University of Duisburg-Essen, Duisburg, Germany.

The interest in perovskite solar cells is growing rapidly due to their versatile applicability for energy harvesting systems. In a short period of time, devices already reached efficiencies up to 22%, making them comparable to established thin-film solar cells like CuIn(Ga)Se₂ or CdTe. The quantity of publications dealing with planar and rigid solar cells is growing tremendously; however, flexible solar cells have not been in focus yet. Since the 1D structure provides a greater flexibility in comparison to planar systems, applications ranging from e-textiles/wearables to lightweight applications are feasible. Here, the single step fabrication of phase-pure organic-inorganic lead halide perovskite fibers by inert electrosprinning technique is presented. Morphological, as well as optical/photonic properties have been studied and demonstrated first comprehensive data on electrosprun organic-inorganic hybrid materials. Substitution of the absorbing layer in planar heterojunction solar cells with perovskite fibers resulted in a photovoltaic response under simulated sunlight conditions. These flexible 1D hybrid perovskite fibers are potential elements for flexible optoelectronics and mark a starting point towards competitive fibrous solar cells.

ET05.06.11
Dynamics of Trap States in Passivated Halide Perovskite Films Stuart Macpherson1, Andrew J. Winchester2, Tiarnan Doherty1, Christopher Petoukhoff1, Michael K. L. Man2, Keshav Dani2 and Samuel D. Stranks1; 1Department of Physics, University of Cambridge, Cambridge, United Kingdom; 2Femtosecond Spectroscopy Unit, Okinawa Institute of Science and Technology Graduate University, Okinawa, Japan.

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 luminance and device efficiency. We have recently shown that the addition of potassium halides can increase luminescence yields 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 (CsFAMA)Pb(I0.85Br0.15)3 films with < 30 nm spatial resolution. Our results show that chemical passivation by potassium doping reduces the density of surface defects on the films. Confocal photoluminescence maps of fiducially marked sites show a clear anti-correlation between areas of high photoluminescence intensity, and regions of high trap densities based on the photoemission fingerprints. 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.

ET05.06.12
Relation Between Absorption and Electronic Properties of Organic-Inorganic Halide Perovskites Martin Ledinsky1, Tereza Schonfeldova1, Jakub Holosovsky1,2, Zdenka Hajkova1, Lucie Abelova1, Neda Neykova1, Erick Aydin1, Steffan De Wolf3 and Antonin Fejfar1; 1Department of thin films, Institute of Physics AS CR, Prague, Czechia; 2Faculty of Electrical Engineering, Czech Technical University in Prague, Prague, Czechia; 3KAUST Solar Center (KSC), King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

We have probed the temperature dependence of methylammonium lead iodide (CH₃NH₃PbI₃) absorption spectra. We extract the Urbach energy as the reciprocal value of the slope of the absorption at the band edge plotted in logarithmic scale. Its value depends on the material disorder and generally correlates well with the loss in the open-circuit voltage (VOC) of optimized cells, compared to their bandgap [1]. When cooling CH₃NH₃PbI₃ film we find a strong decrease in their Urbach energy and a slow decrease of their optical band gap energy. 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 CH₃NH₃PbI₃ 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 monocristal semiconductors.

We compared the photoconductivity and emission-based absorption spectroscopies, we find that the CH₃NH₃PbI₃ band structure is slightly indirect. This
Feasibility of Quantum Dot Based Lasers in Blue and Green Region

Arpna S. Shinde, Amruta A. Lohar, Richa Gahlaut and Shailaja Mahamuni;
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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 biexcitonic recombination. The sign of stimulated emission is observed under low excitation of xenon lamp (~ 4.16 mW) and is the effect of high biexcitonic binding energy (40 meV) which avoids the re-absorption of biexcitonic photon in excitonic peak.

In addition to the PL yield, we have studied the PL decay time of our CsPbBr3 and CsPbCl3 QDs at low temperature. By changing the halide composition from CsPbBr3 to CsPbCl3, the QDs can emit tunable emission across the blue to green region. The PL decay time is measured by lifetime and decay constant which can be used to tune the lasing wavelength. We have used our QD to tune the wavelength from 400 to 700 nm.

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.

References


ET05.06.13

Feasibility of Quantum Dot Based Lasers in Blue and Green Region

ET05.06.14

Efficient NTSC Blue and White Perovskite Light Emitting Diodes via Mn Doping at B-Site

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Lead halide perovskites 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 2Blue 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 %. 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:PF1), we achieved ~7 fold increase in the efficiency to 0.5%. Further, we improved the quality of nanocrystals by doping with Mn, which eventually lead to a factor of 4x enhancement in the EQE (2.1%) with a FWHM of 17 nm, meeting the standards of pure NTSC blue coordinates. We then used down converting green and red nanocrystals to construct all perovskite white LEDs for the first time. In this presentation, I will discuss the evolution of blue nanocrystals in LEDs and the impact of Mn doping on their PLQY and device performance.

References


ET05.06.15

Acid-Catalyzed Reactions Activate Solvents in Perovskite Precursor Inks

J. C. Hamill1, Jeffrey Schwartz2 and Yueh-Lin (Lynn) Loos3;
1Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, United States; 2Department of Chemistry, Princeton University, Princeton, New Jersey, United States; 3Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States.

Hybrid organic-inorganic perovskites (HPs) have revolutionized the field of photovoltaic (PV) devices. HPs with mixed cations, specifically those comprised of combinations of formamidinium, methylammonium (CH3NH3+) and cesium cations, have resulted in devices with record-setting efficiencies. 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.

References

(CH$_3$)$_2$NH$_3$I confirms that substitution of CH$_3$NH$_3+$ with (CH$_3$)$_2$NH$_2+$ alters the perovskite structure. When CH$_3$NH$_3$I is the sole organoammonium iodide in the precursor solution, the formation of (CH$_3$)$_2$NH$_2$I and its subsequent incorporation in thin films produces a cubic-phase film instead of the conventionally accessed tetragonal-phase CH$_3$NH$_3$PbI$_3$. Interestingly, devices that incorporate such cubic-phase films exhibit enhanced stability towards humidity compared with devices with the more conventionally accessed tetragonal CH$_3$NH$_3$PbI$_3$. Our study emphasizes the importance of precise control over solution chemistries; the by-product(s) of which, when incorporated in the solid state, can result in structural differences that can ultimately impact macroscopic properties and performance.

ET05.06.16
Metal-Halide Perovskite Quantum Dots in Nanoporous Thin Films for Optoelectronic Applications Stepan Demchyshyn, Serdar Sariciftici, 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 regime. 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

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 photoresponse 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 Yehonadav Bekenstein$^{1,2}$, Nanjia Zhou$^3$, A. P. Alivisatos$^1$ and Jennifer Lewis$^3$; $^1$Chemistry, University of California, Berkeley, Berkeley, California, United States; $^2$Material Science, Technion–Israel Institute of Technology, Haifa, Israel; $^3$School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

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>confined effects, making them attractive candidates for a wide range of electronic and photonic applications.
applications. The ability to precisely pattern one-dimensional nanomaterials with controlled spatial orientation into planar and 3D structures that exhibit highly anisotropic properties would open avenues for the integrated design and assembly of optoelectronic devices. Towards this goal, we created stable nanocomposite inks composed of brightly emitting colloidal cadmium lead halide perovskite (CsPbX₃, X = Cl, Br, and I) nanowires suspended in a polystyrene-polyisoprene-polystyrene block copolymer matrix. Using direct ink writing, we programmatically controlled the nanowire alignment within these matrices to produce photonic nanocomposites that exhibit highly polarized absorption and emission properties. Using this approach, we created several device motifs for optical storage, encryption, sensing, and full-color displays as exemplary demonstrations. The polymer encapsulated perovskite nanowires exhibit increased stability towards air and moisture degradation process, suggesting the methods and materials we use can be implemented in future devices.

ET05.06.20
All-Solution Processed Perovskite Light-Emitting Devices Teajun Kim¹,², Jin-Hoon Kim¹ and Jin-Woo Park¹; ¹Yonsei University, Seoul, Korea (the Republic of); ²Samsung Electronics, Seoul, Korea (the Republic of).

As research on perovskites has rapidly developed in recent years, various research groups have made great efforts on improving the process 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 polyvinyleneimine (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 (Cs₃CO₃, Alq₂, and CsF) were selected as n-type dopant. Also, thin layer of polymethylmethacrylate (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.

ET05.06.21
Impact of Excess PbI₂ on the Structure and the Temperature Dependent Optical Properties of Methylammonium Lead Iodide Perovskites Fabian Panzer¹, Tobias Meier¹, Tanaji Gujar¹, Andreas Schönleber¹, Selina Oltho², Klaus Meerholz², Sander van Smaalen¹, Mukundan Thelakkat¹ and Anna Kohler¹; ¹Univ of Bayreuth, Bayreuth, Germany; ²University of Cologne, Cologne, Germany.

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.

ET05.06.22
Broadband Luminescence in Small Molecule Engineered Hybrid Perovskites Shreya Krishnamurthy¹,², Rounak Naphade², Suresh Gosavi¹, Sudip Chakaborty³, Ramanathan Vaidhyanathan³ and Satsishandra Ogale³; ¹Department of Physics, Savitribai Phule Pune University, Pune, India; ²Department of Physics, Indian Institute of Science Education and Research (IISER), Pune, India; ³Uppsala University, Uppsala, Sweden; ⁴Indian Institute of Science Education and Research (IISER) Pune, Pune, India.

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, 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 (H₃N-CH₂-CH₂-NH₃)₈(Pb₄Br₁₈)●Br₆ as well as 2D corrugated system of (H₆N-CH₃-CH₂-NH₃)(Pb₃Br₁₃)●Br₆, as well as 2D corrugated system of (H₆N-CH₃-CH₂-NH₃)(Pb₃Br₁₃)●Br₆, where the common amine used was ethylene diamine (En), which is the smallest amine 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.

ET05.06.23
Electronic Structure Analysis of an Organometallic Halide Perovskite via Photoemission Yield Spectroscopy in Air at Various Temperature Around the Phase Transition Temperature Daisuke Yamashita¹, Yoshiyuki Nakajima¹, Satoshi Uchida² and Hiroshi Segawa²; ¹RIKEN KEIKI Co., Ltd., Kasukabe, Japan; ²The University of Tokyo, Tokyo, Japan.

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, PYSAs measurement was performed as follows. UV light emitted from a deuterium lamp was monochromatized using a grating monochromator, which was then focused on 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, PYSAs 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 semiconductor 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 Parimongkol1, Nabeel S. Dahod2, Alexia Stollmann1,2, Shao-Liang Zheng4 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; 4Chemistry, 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 Lindenbergl; 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 corresponding 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 it’s “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 both 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.

ET05.07.01
Instability of Lead Halide Perovskites Yabin Qiu; 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 deeper 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.

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.

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 FAPO₄, 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 $V_{oc}$ 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 materials 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 revaluated 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) McKeen 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) Gholidpour, ...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 CH$_3$NH$_3$PbI$_3$ Single Crystal
Qianniu Lv and Qingfeng Yan, Tsinghua University, Beijing, China.

As a new semiconductor material, methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$) perovskite has attracted much attention in recent years owing to its outstanding photoelectric properties. Although CH$_3$NH$_3$PbI$_3$ 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 CH$_3$NH$_3$PbI$_3$ perovskite. In this work, we report the fast growth of high-quality CH$_3$NH$_3$PbI$_3$ single crystal by using a non-seeded solution growth method. When exposed the CH$_3$NH$_3$PbI$_3$ 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 CH$_3$NH$_3$PbI$_3$ 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 CH$_3$NH$_3$PbI$_3$ single crystals. Vertical-structured FET devices based on CH$_3$NH$_3$PbI$_3$ 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 CH$_3$NH$_3$PbI$_3$ 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-Perez2, Matthew Leyden1, 4, Yuchi Kato1, 5, Mikas Remeika1, 6, Shenghao Wang1, 7, Michael V. Lee2, 8, Andrew J. Winchester2, Atsushi Gabe1, 9, Yan Jiang1 and Yabing Qi1; 1Okinawa Institute of Science and Technology, Okinawa, Japan; 2Department of Energy Materials and Surface Sciences Unit, Okinawa Institute of Science and Technology (OIST), Okinawa, Japan; 3Department of Engineering and Physics, Karlstads University, Karlstad, Sweden; 4Melbourne Centre of Nanofabrication, Monash University, Melbourne, Victoria, Australia; 5Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka, Japan; 6CNT-Application Research Center, National Institute of Advanced Industrial Science and Technology (AIST), 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 Science Unit has been making concerted efforts to study 2-D, 3-D “tetrais[(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(trifluoromethanesulfonfonyl)imide (LITFSI), 4-tert-butylpyridine (t-BP) and spiro-MeOTAD. Also, we will show how gas exposure (e.g., exposure to O$_2$, H$_2$O, N$_2$) 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 ~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 \textit{in situ} monitor the transformation of organohalide perovskites from precursors to final films upon thermal annealing at different relative humidity. \textit{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 \textit{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 oriented 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$_3$PbI$_3$-Cl$_x$ undergo rapid degradation when exposed to oxygen and moisture. To overcome this problem, many researchers have been studying 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, 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 provide an efficient separation of electrons and hole as well as be responsible for increased non-radiative recombination [2,3]. There have been relatively few theoretical predictions of GBs and these have thus far only focussed on MAPbI$_3$ and associated intrinsic defects [4,5].

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$_4$[6-8]. 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

Jue Gong1, Mengjin Yang3, Dominic Rebollar1,2, Peijun Guo2, Jordan Rucinski2, Zachary Liveris1, Richard D. Schaller2,4, 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 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

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 (OIHPs) 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 OIHP thin films over large areas is critically important. The microstructures and grain-boundary networks in the resulting polycrystalline OIHP thin films are equally important as they control the device performance and stability. Fundamental phenomena pertaining to synthesis, crystallization, coarsening, microstructural evolution, and grain-boundary engineering involved in the processing of OIHP 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; 2College of Chemistry, University of California, Berkeley, California, United States; 3Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Chemistry, Northwestern University, Evanston, Illinois, 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 are able to characterize and monitor fast reaction/formation of perovskite thin films 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 influences 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-CI 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
Savayant Sasmal1, 2, Raj Pala2, Sri Sivakumar2 and Suresh Valiyaveetil1, 3National 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 perovskite promising. Having contender for double junction tandem solar cell useful to achieve much higher efficiency (theoretical efficiency limit 46.1%) than single junction solar cell (efficiency limit 33.7%). Although several methods such as simple exchange of alkyl halides, compositional substitution, variation of precursor solution concentration, aliovalent doping as well as osmotic swelling induced fragmentation exists to tune the band gap of hybrid perovskite originated in solution phase, none of them applied in case of band gap tuning in recently acclaimed gas induced growth of hybrid perovskite due to lesser flexibility to implement all these methods in gas induced reaction impeded its use in multi junction tandem solar cell. Formation of ultra-smooth film, facile quantum confinement and most importantly large area fabrication established an unassailable importance of gas induced growth process in hybrid halide perovskite field, albeit limited in use in double junction tandem solar cell due to inability to tune the band gap.

In the context of band gap tuning of methylammonium lead iodide (MAPbI3) in gas induced growth, here we introduced a complete mechanistic detail highlighting a new synthetic route depicting selective adsorption (of in situ formed hexylamine on the Pb site of growing MAPbI3) induced anisotropic growth of MAPbI3 leading to a unique sheet like structure of much higher band gap (2.18 eV). Moreover, gradual evaporation of in situ formed free hexylamine from the solvated intermediate and simultaneous relaxation of growth restriction on MAPbI3 during prolonged exposure of hexylamine 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 will 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 phase segregation of the materials under light illumination. In this talk I will explain how these issues can be addressed via multi-scale material modification combining composition tuning, grain engineering and surface passivation. Firstly, I will introduce a new mechanism to suppress ion migration in bulk perovskites through the interstitial incorporation of small alkali cations in the lattice of the state-of-the-art Cs/MA/FA triple cation perovskites. Through a combined experimental and theoretical investigation on the incorporation of extrinsic alkali cations (Rb+, K+, Na+, and Li+) in the perovskite materials, we unambiguously reveal the size-dependent interstitial occupancy of these cations in the perovskite lattice and demonstrate increased ion 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 FA\textsubscript{0.8}Cs\textsubscript{0.2}PbI\textsubscript{3-x}Br\textsubscript{x} (0 ≤ x ≤ 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)\textsubscript{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%, 1.296V/15.01% and 1.312V/14.35% for WB-OIHPs 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 photoemission, 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
Yehao Deng1, 2 and Jinsong Huang1, 2; University 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.
The surfactant additives enabled the deposition of uniform, full-coverage perovskite film at a coating rate of 180 meter per hour and resulted in stabilized module efficiencies of 15.3% and 14.6% measured at aperture areas of 33.0 and 57.2 square centimeter, respectively. The result indicates that surfactants could be a kind of general additives in perovskite inks for improving perovskite film quality in scalable solution coating methods.

4:45 PM ET05.08.07

Two dimensional metal halide perovskites have demonstrated exceptional stability and performance in various optoelectronic applications. A key to improving the 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 Clark1, Liangliang Liang1, Ran Tao1, Xinwei Guan1, Ali Han1, Xiaogang Liu1, Lain-Long Li1, Mark C. Hersam1, 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 perovskites (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 (MA1-xFAx)0.39Pb0.727I3.844 perovskites, which sequentially enhance photovoltaic performance characteristics. Optimised transistors are shown to combine low voltage operation (-1 V) with high carrier mobility (32.25 cm2/Vs) and exceptionally high channel current ON/OFF ratio (107). 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. Schueller1, Oleg Kontsevoi, 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)1-x(M)n-x(I)3+x(en)x. (en = ethylenediammonium (MA), formamidinium (FA); M = Sn, Pb, en = ethylenediammonium)3-4. Incorporation of en cations in the 3D perovskite structure leads to massive M and I vacancies in the 3D [MX3] 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)0.81(en)0.19Sn0.02(I)2.823 perovskite is stable in air for at least 9 days, while the (FA)0.84(en)0.16(Pb)0.03(I)2.943 perovskite is stable in air for more than 300 days. Both lifetimes are the highest reported for a 3D SnX3 and a 3D FAPEI 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
Recently, perovskite LEDs are 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)x(MA)yPbBrz+1 has 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), benzytrimethylammonium (BTA)) 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)x(MA)yPbBrz+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.

**ET05.09.03**

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

In this work, we studied the photocarrier-induced refractive index change in organic-inorganic hybrid perovskites. The crystal used in this study was a large-size single crystals of halide perovskites can be grown in low-temperature solution exhibiting high optical transparency and exceptionally low surface roughness. 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 roughness. These optical properties are beneficial for novel optical transmittance 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 large-size single crystals of halide perovskites. 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 measurement 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.

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**ET05.09.06**

**A Device Simulation of Organohalide Perovskite Resistive Random Access Memory**

Kyunghwan Min, Sungwoo Cho and Yongwoo Kwon; Hongik University, Seoul, Korea (the Republic of).

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 Lee1; 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 (I-V) 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 Rashaa A. Awni, Changlei Wang, Xinxing Yin, Zhaoqing 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 (PVSCs) 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, Cu(In, Ga)Se₂, etc.) and organic thin film solar cells, and has recently been used to characterize PVSCs. Interestingly, some unique trap signatures were observed in the AS measurements of PVSCs, 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/C₆₀-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 ETL/HTLs. The devices exhibit different capacitance signatures, indicating that defect states probed 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 concentration on the optical properties of perovskites. Our finding will eventually lay-down a platform for high performance, Pb-less perovskite light emitting diodes.

References

ET05.10.10
Environmental Gating and Galvanic Effects in Single Crystals of Methylammonium Lead Bromide Perovskite Mahshid Ahmadi1, Eric Muckley2, Ilia Ivanov2, Eric Lukosi3, Jeremy Tisdale1, Ivan Kravchenko2, Sergei V. Kalinin2, Bin Hu1 and Liam Collins2; 1Joint Institute for Advanced Materials, University of Tennessee, Knoxville, Tennessee, United States; 2Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3Nuclear Engineering, The University of Tennessee, Knoxville, Tennessee, United States.

Understanding the impact of environmental gaseous on the surface chemistry of organic-inorganic perovskite couples to the electronic and ionic transport is critically important. Here, 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 gas response of MAPbBr3-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 N2 and O2 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 environment, 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−Br pair that defines the bulk conductivity of MAPbBr3 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 Wang1, 2, 3, Alex M. Ganose2, 3, 4, Chunning Niu1 and David O. Scanlon2, 3, 4; 1School of Electrical Engineering, Xi'an Jiaotong University, Xi'an, China; 2Department of Chemistry, University College London, London, United Kingdom; 3Thomas Young Centre, University College London, London, United Kingdom; 4Diamond 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. 2D hybrid halides perovskites which feature long chain alkylammonium cations are generally suggested for light emitting diode applications, due to their strong photoluminescence (PL), 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)PbX3 (X = Cl, Br, I), the energy transfer and charge separation between organic and inorganic components of the structures are still not fully understood.

Herein, we investigate the geometrical, electronic and optical properties of the semiconducting 2D perovskites (AEQT)BX4 (B = Pb, Sn; 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)PbCl4, (AEQT)PbBr4, (AEQT)PbI4 and (AEQT)SnBr4, 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)SnI4 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)SnI4 is a promising class of stable and efficient light-absorbing materials for photovoltaics.


ET05.09.12

New Electron Transporting Materials for Perovskite LED Seekwoo Kang, Yeonhee Sim, Beomjin Kim and Jongwook Park; Kyung Hee University, Yongin, Korea (the Republic of).

In conventional organic light emitting diode (OLED), aluminium quinoline (Alq3) has been widely used as an electron transporting layer (ETL) in the past. And in the perovskite light emitting diode (pLED) device, 1,2,2′,2″-tetrais(3,5-benzentriyl)-1,2′,2″-tris(phenyl-1-H-benzimidazole) (TPBi) has been generally used as an ETL because it has better ETL property based on the higher electron mobility than Alq3 in the device. However, TPBi has disadvantage in terms of device life time compared to the Alq3 because of the inferior thermal property. Therefore, we designed and synthesized new organic electron transporting materials for perovskite light emitting diode (pLED) which includes thiadiazolo[5,4-b]pyridine and benzene|quinoline moieties, respectively. We report the pLED device performance having new two ETL compounds as well as TPBi. The device configuration is ITO/PEDOT:PSS-PSS:Na/perovskite of materials for perovskite light emitting diode (pLED) deivice, 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) has been generally used as.

ET05.09.13

Continuously Tunable Photoluminescence of Two-Dimensional Layered Perovskite Semiconductors Under High-Pressure Sheng Liu1, Shishuai Sun1, Chee Kwan Gan1, Jun Xing1, Thu Ha T. Do1, Andres T. Granados del Aguila1 and Qihua Xiong1; 1Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore; 2Tianjin University of Technology, Tianjin, China; 3Institute of High Performance Computing, Agency for Science, Technology and Research, Singapore, Singapore.

Organic-inorganic hybrid semiconductors with a perovskite lattice have recently attracted great attention due to their extraordinary performance in photovoltaics and excellent light-emission properties. Among them, unique layered structures exist building up from atomically thick quantum wells, each of which has one layer of inorganic octahedra that is sandwiched by organic layers of long chain ligands. As a result, couple electron-hole pairs (excitons) experience strong dielectric confinement, leading to tightly bound excitons with strong emission even up to room temperature. In this work, pressure induced changes in the optical emission of two-dimensional perovskite crystals (PEA)PbI3, has been systematically studied at room temperature by several 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 Patternning 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 nanoscale patterning of perovskite films which is one of the most critical issues for large area and 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, polystyryl-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_{P2VP}) and the amount of perovskite, the effective volume fraction (f_{P2VP}) 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, nanoscale patterning of perovskite 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 Tetzuka1, Tomoko Inose2, Hiroshi Uji-i2, Satoshi Asakura2 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 optoelectric properties such as long carrier diffusion length, am-bipolar conductivity, broad color-tunability exchanging 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 a next generation and solution processable semiconductor materials. Recently, bright luminescence from methylammonium lead tri-bromide (MAPbBr3) perovskite nanocrystals (PeNCs) has been reported owing to the development of methods for preparing these PeNCs. Especially, MAPbBr3 PeNCs were prepared by ligand-assisted reprecipitation (LARP) inspired by the reprecipitation 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.

References
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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; Department of Materials Science and Engineering, Yonsei University, Seoul, Korea (the Republic of).

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, ClBr3-a, and BrI3-a) 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 repopulates 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
ET05.09.17
Anisotropic Excitons in Two-Dimensional Layered Lead Halide Perovskite Semiconductors Thu Ha T. Do, Andres T. Granados del Aguila, Jun Xing, Sheng Liu, Chongyung Jiang, Weibo Gao and Qhui Xia Xiong; Nanyang Technological University, Singapore, Singapore.

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 nanostucture 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)2PbI4 crystals. Four intrinsic optical transitions are resolved in the luminescence spectrum, originating from the radiative recombinantion 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 Sayantan Sasimali1,2; Sri Sivakumar1, Raj Pala' and Suresh Valiyaveettil1; IIT Kanpur, Kanpur, India; 1Chemistry, National University of Singapore, Singapore, Singapore.

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 restructuration 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 (MAPbI3) associated with structural transformations and then developed a generic mechanistic route on interaction of ammonia (NH3) 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 NH3) 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 NH3 gas. The mechanistic study addresses three important factors such as quick response, reversibility, and stability of perovskite materials in the presence of NH3 gas, which could lead to the design of stable and sensitive two-dimensional hybrid perovskite materials for developing sensors.

ET05.09.19

Using ABX3, 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 comparably more controlled manner. We report on CMS to form MAPbI3(1,Brxmy), 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 ~100 nm depending on the composition (for MAPbI3,MArxCsryPbzI3 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 2θ = 29.63° - 30.02°, i.e., from the neat MAPbI3 (220) towards 2θ =30.02°, 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 MAxRb(1-x)PbI3, MAxCs1-xRb1-xPbI3, and MAxCs1-xRbyPbzI3 were synthesized. We will report on characteristics of both the films alone, and of PV cells with architecture FTOTiO2|meso-TiO2|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 Hyoung-Do Kim and Hyun-suk Kim; Materials Science and Engineering, Chungnam National University, Daejeon, Korea (the Republic of).

Low-cost hybrid organic-inorganic perovskites such as methylammonium lead iodide(MAPbI3) 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 MAPbI$_3$ active layer were investigated. MAPbI$_3$ thin-film deposited by chemical vapor deposition (CVD) with MAI and PbI$_2$ sources, and its physical, chemical, optical properties were compared with the solution-processed MAPbI$_3$ thin-film. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) revealed that solution-processed MAPbI$_3$ thin-film was easily transformed (from MAPbI$_3$ to PbI$_2$) after 7 days when exposed to air. However, CVD-grown MAPbI$_3$ 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 MAPbI$_3$ thin-film has large grain size and small surface roughness as compared to solution-processed MAPbI$_3$. MAPbI$_3$ 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 MAPbI$_3$ phototransistors were examined for the optoelectronic application.

**ET05.09.21**

Dipolar Disorder, Localized Charges and Their Effect on Charge Transport in Perovskites

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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 CH$_3$NH$_3$PbI$_3$, 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 CH$_3$NH$_3$PbI$_3$ 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 CH$_3$NH$_3$PbI$_3$ the mobility and the half-lifetime increase by a factor of three to six 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 (CH$_3$NH$_3$+) 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

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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-and-dielectric-confined nature makes colloidal lead bromide perovskite nanoplatelets a favorable candidate for the next-generation deep-blue-emitting (470 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 prepared precursor solutions for ligand-assisted reprecipitation is critical 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 drop-casted 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

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All-inorganic cesium lead halide perovskites quantum dots (QDs), CsPbX$_3$ (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 anion exchange of Pristine CsPbX$_3$ QDs using ammonium iodide salts, long alkyl based oleylammmonium iodide (OAMI) and aryl 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 CsPbBr$_3$/I$_3$ films exhibit a strong red shift in their 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 CsPbBr$_3$/I$_3$ led to the transformation of perovskite 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 CsPbBr$_3$/I$_3$ film based on OAMI shows a high surface coverage ratio and is free of pinholes, whereas that of AnHI based CsPbBr$_3$/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 BT.2020 color gamut. Similarly, the LEDs formed using the QDs based on AnHI 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).

Reference:
(2) T. Chiba et al., ACS Appl. Mater. Interfaces, 2017, 9, 18054.

ET05.09.24
What Limits the VOC of Br-Based Perovskite Solar Devices? David Cahen1, Arava Zohar2, Michael Kulbak1, Igal Levine1, Gary Hodes3 and Antoine Kahn4; 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 (EC-VOC) of ~ 0.4 V. Unfortunately, up to now, for the higher bandgap HaPs, where the halide is only Br, the highest reported VOC still leaves (EC-VOC) ~ 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 EC-based cell for tandem configurations or spectral splitting systems. The origin of this increased loss remains an open question. There are 3 main issues to be checked to understand what limits the VOC from getting closer to the theoretical maximum value for pure APbBr3-based PV cells (~2.0 V).

1- what is the absorber’s in-gap density of states and what range of energies have these states in the material’s band gap;
2- as 1-1, for interfacial in-gap states at the HaP-hole/-electron transport layer interface;
3- what is the mismatch in energy level alignment of the cell’s layers, to see if this can explain the significant energetic losses?

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 high and fast optical nonlinear effects owing to the enhancement of electron density of states and electron-electron interaction. Among the lead halides 1D cells and light emitting diodes because of their excellent electronic properties including strong absorption coefficient and long carrier lifetime [1]. The organic-inorganic lead halide hybrid perovskites have been receiving considerable attention for applications to optoelectronic devices such as photovoltaic cells and light emitting diodes because of their excellent electronic properties including strong absorption coefficient and long carrier lifetime [1]. The structure of hybrid perovskites can be tuned in various manners and classified by dimensionalities into three-, two- and one-dimensional (3D, 2D, and 1D) perovskites. Compared with 3D and 2D-layered crystals, the limited number of studies have been done for 1D crystals, while they are expected to show high and fast optical nonlinear effects owing to the enhancement of electron density of states and electron-electron interaction. Among the lead halides 1D perovskites, we have found that bromide compounds show some advantages for applications: stability in air and broadband emission of light. Here we report the structure of 1D lead bromide perovskites and structural dependence on their optical properties. We prepared three different structures (triple-chain, face, and side shared) by inserting various aromatic organic compounds. We observed the yellow, green, and white light luminescence depending on the structures of lead bromide perovskites. Among them, triple-chain lead bromide perovskite crystal showed extremely broadband white light photoluminescence similar to that of core-shell quantum wires structure [2]. The Stokes shift of the triple-chain lead bromide crystals examined in the present experimental was much larger than that reported previously for core-shell 1D wires. The results open possibility of new application of 1D bromide perovskites to optoelectronic devices on the basis of chemical modification.


ET05.09.26
Structure-Controlled Optical Thermoresponse in Two-Dimensional Perovskites Daniele Cortechia1, Stefanie Neutzner1, Jun Yin2, Teddy Salim3, Ajay Srinath Kandada1, Annalisa Bruno1, Ying Ming Lam1, Javier Martí-Rujas1, Annamaria Petrozza1 and Cesare Scoci2; 1Centre for Nano Science and Technology, Istituto Italiano di Tecnologia, Milan, Italy; 2Solar Center, Division of Physical Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia; 3School of Material Science and Engineering, Nanyang Technological University, Singapore, Singapore; Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore, Singapore; Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore.

Two-dimensional perovskites are emerging for their light emitting properties and applications in lasing, metamaterials and nanophotonic devices. The correlation between structure and optical properties is essential to improve the device performance and functionality and might lead to perovskite films with adjustable optical properties dynamically tunable by external stimuli. Phase transitions in Ruddlesden-Popper perovskites such as (BA)2(MA)n-2(PbI2n+1) (BA = butylammonium; MA = methylammonium),1,2 in combination with the high flexibility of the lead halide lattice, can allow to modulate the optical properties in a controlled and reversible way. However, a thorough correlation between the structural-induced induced changes and the optical properties is not yet established. Here, we expose BA2PbI4 (n=1) and BA3MAPb3I10 (n=2) to a wide temperature range (300-77K) and characterize two new low temperature phases of BA3MAPb3I10. We combine spectroscopic and structural characterization with ab initio calculations to study their characteristic phase transitions and rationalize the structural changes affecting the optical properties and leading to a sharp thermo-optical response of their luminescence. Volume contraction at low temperature causes the increase of out-of-plane tilt of PbI6 octahedra resulting in a sharp bandgap blue-shift. On top of this, the dimensionality further impacts on the thermal evolution of the volume expansion and tilt system of the perovskite, reversing in BA3PbI10 the trend of the continuous...
thermal shift of the band-gap typically observed in MAPbI3. Our results stress the importance of the structure-function relationship and show that heat-mode inter-conversion of the crystal packing can be exploited to design stimulus-responsive materials. Since the β→α phase transitions of these alkylammonium-based perovskites occur close to room temperature, they can be easily exploited to switch the structure-optical properties of the material.


ET05.09.27

Choice of Monovalent Cations Has Major Impact on Charge Carrier Recombination in Metal Halide Perovskites Katelyn Dagnall², Benjamin Foley², Shelby Cuthrief², Matthew Alpert¹, Xiaoyu Deng¹, Tianran Chen¹, Seung-Hun Lee¹, Yingzhong Mai¹ and Joshua Chor²; ¹University of Virginia, Charlottesville, Virginia, United States; ²Chemical Engineering, University of Virginia, Charlottesville, Virginia, United States; ³Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

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.

ET05.09.28

Photoluminescence Intermittency in Micron-Sized Hybrid Lead Halide Perovskites Shabial Sarkar; IIT Bombay, Mumbai, India.

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 crystallite 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 photoelectronically 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 nanoparticle

ET05.09.29

The Formation of Cs4PbI6 and Its Effect for Device Characteristics in CsPbI3 Based Perovskite Solar Cells Kohei Yamamoto1, Tetsuhiko Miyadera1, Tomoyuki Koganezawa1, Tetsuya Taima2 and Masayuki Chikamatsu1; 1AIST (National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 2Kanazawa University, Kanazawa, Japan; 3JASRI, Sayo-gun, Japan.

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 efficient optoelectronic and electrical properties. It should also be noted that the reported CsPbI3 perovskite solar cells with highly efficiency has Cs4PbI6, 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 Cs and PbI2. The ratio of the codeposition rates of PbI2 and CsI was adjusted to PbI2/CsI molar ratio. The CsPbI3 film of PbI2/CsI molar ratio of 1 was deposited for obtained ideal stoichiometry 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, an 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 constitution of 3CsI and PbI2 with CsI. The CsPbI3 film of PbI2/CsI molar ratio of 1 was deposited for obtained ideal stoichiometry of CsPbI3. In this case, a power conversion efficiency of 3.77% was obtained with a short-circuit current density (Jsc) of 11.50 mA/cm2, an open-circuit voltage (Voc) of 0.55 V, and a fill factor (FF) of 0.39. These results indicated the effect of Cs4PbI6 to improve the solar cell performance (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 Cs1AgBiBr6 Laura Schade, Adam D. Wright, Roger Johnson, Markus Dollmann, Pabitra Nayak, Dharmalingam Prabhakaran, Laura Herz, Robin Nicholas, Henry Snaith and Paolo Radaelli; University of Oxford, Oxford, United Kingdom.

The discovery of hybrid halide perovskite 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 bio electronics 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 A2BB′X6 (A, B=monovalent

Recently, observations of twin domain in methylammonium lead triiodide (MAPbI₃) have drawn significant attention. However, whether this twin domain correlates well with the phase transition. Further absorption and photoluminescence spectral measurements probing the temperature dependence of the indirect bandgap transition will also be reported.

We have investigated the temperature-dependent structural behaviour of Cs₃AgBiBr₆ using heat capacity measurements, X-ray powder and single-crystal diffraction and neutron powder diffraction and discovered that this compound undergoes a low-temperature structural phase transition (T_c=122 K) from cubic to tetragonal. The crystal structures of both high- and low-temperature phases were refined based on our diffraction data. The temperature dependence of the exciton energy in proximity to the direct band gap was determined using reflectivity measurements. We found a direct, linear relationship between the tetragonal strain and the exciton energy, demonstrating that the latter is controlled by the BiBr₆ octahedral rotation. Meanwhile time-resolved photoluminescence measurements indicated a qualitative change in the charge-carrier recombination mechanisms at a temperature that correlates well with the phase transition. Further absorption and photoluminescence spectral measurements probing the temperature dependence of the indirect bandgap transition will also be reported.

ET05.09.31
Investigation of Bismuth Based Perovskite Thin Film for Solar Cell Application
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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 opto-physical 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.

ET05.09.32
Photoelectrochemical Impedance Measurement on Perovskite Solar Cells with Improved Thermal Stability
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Recently, photoelectrochemical 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. However, there are still elusive phenomena and the impedance response is not fully understood. Basically, two main processes are identified but there is no general agreement on their physical origin. Negative loops that appear in the medium and low frequency ranges further complicate a straightforward interpretation of the impedance response of PSC.

Here, we present a case study of a PSC based on a new compound material (MA₂ₓFₓAgₓPb₁₋ₓBr₃) that does not show a phase transition for relevant ambient conditions and has proven to exhibit better thermal 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 photocative 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.

ET05.09.33
Chemical Nature of Ferroelastic Twin Domains in CH₃NH₃PbI₃
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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 mechanical 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 (HIM-SIMS) and nanoscale infrared spectroscopy
Furthermore, we found that two independent trion generation pathways exist by analyzing the excitation power dependence of trion components. We clarified that the generation of trions are clearly influenced by the polycrystalline grain structure, making it difficult to measure intrinsic properties [1]. Thus, 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).


ET05.09.35

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

Lyming Dong, Jianfeng Zang, Lei Ye and Zhao Chen; Huazhong University of Science and Technology, Wuhan, China.

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 CsPb0.8Mn0.2Cl0.95I0.05 and CsPb0.8Mn0.2Cl0.4Br0.6 QDs at 100°C in the air with high Mn substitution ratio, up to 55.64% atomically. The as-prepared CsPb0.8Mn0.2Cl0.95I0.05 QDs exhibit high PLQYs of 62.41% and dual-color emission with two strong emission peaks around 400 - 460 nm and 600 nm, respectively. Furthermore, the unique advantage of the optical emission and high PLQYs properties of the CsPb0.8Mn0.2Cl0.95I0.05 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.

ET05.09.36

Understanding Effects of Precursor Solution Aging in Triple Cation Lead Perovskite

Passarut Boonmongkolpras, Daehun Kim1, Esra Alhabshii2, Issam Gereige2 and Byungha Shin1; 1Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Saudi Aramco Research & Development Center, Dhahran, Saudi Arabia.

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 performance. 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.

ET05.09.37

Nonlinear Optical Properties of MAPbCl3 Perovskite Single Crystals

Keiichi Ohara, Takumi Yamada, Hirokazu Tahara, Tomoko Aharen, Hideki Higiri and Yoshihiko Kanemitsu; Kyoto University, Uji, Japan.

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 single crystals used in this study were synthesized with an iodine catalyzed solid state reaction, and single crystals were grown with salt flux methods. Structural, chemical, and in depth optical and X-ray spectroscopic study of Ruddlesden-Popper series of the perovskite sulfide, $\text{Ba}^{n+1}\text{Zr}_{n}\text{S}_{n+1}$ ($n \geq 1$). 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. 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 $\text{MAPbCl}_3$. 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

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 mobility 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 $\text{V}$ exhibit typical features of 0-D perovskites, such as low carrier mobilities and strong quantum confinement, thereby limiting their applications in optoelectronic devices. $\text{Sb}$ and $\text{Bi}$ 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 $\text{Sb} 5s$ orbital and $\text{Br} 4p$ orbital in $\text{ASbBr}_6$, 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 Li2, Elisabeth Bianco2, Wei Li1, Michael McConney1, Ralf Haiges5, Anderson Janotti6, David Singh7, William Tisdale3, Rafael Jaramillo4, Rehan Kapadia5, and Jianwei Zhang2; 1Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States; 2Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Department of Physics and Astronomy, University of Missouri, Columbia, Missouri, United States; 4Department of Chemistry, Rice University, Houston, Texas, United States; 5Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, United States; 6Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, 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, $\text{Ba}_{n+1}\text{Zr}_{n}\text{S}_{n+1}$ ($n \geq 1$). 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:
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 photoconductivity 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$_{(1-x)Br_x}$ Anthony Ruth$^1$, Michael C. Brennan$^1$, Sergiu Draguta$^1$, Yuri Morozov$^1$, Maksym Zhukovskyi$^1$, Boldizsar Janko$^1$, Peter Zapf$^1$ and Masaru Kuno$^1$; $^1$University of Notre Dame, South Bend, Indiana, United States; $^2$Argonne National Laboratory, Argonne, Illinois, United States.

Solution-processed mixed halide perovskites (e.g. MAPb$_{(1-x)Br_x}$) 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$_{(1-x)Br_x}$ 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 promotes its application to fundamental, experimentally-inmutable 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$_{(1-x)Br_x}$ (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 managing 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$^1$, Minggang Ju$^2$, Xiao Cheng Zeng$^2$, Yuanyuan Zhou$^1$ and Nitin Padture$^1$; $^1$Brown University, Providence, Rhode Island, United States; $^2$Department 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 perovskite 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$_5$Ti$_3$, Rb$_6$Ti$_4$, K$_2$Ti$_4$, and In$_6$Ti$_4$, which possess optimal bandgap and suitable absorption. Here, we successfully synthesized the Titanium-based materials which indicates plausible photovoltaic applications because of the proper band-gap range. Furthermore, we prepared the pinhole-free titanium-based thin film by the evaporation method. The electrons/holes diffusion length of such thin films with proper crystallographic textures illustrates indicated the possible plausible photovoltaic applications because of the proper band-gap range. 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.

9:45 AM BREAK

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

The outstanding photophysical properties of APb$_X$ 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 diversity and structure, 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. SnF2(DMSO)2 doping to the 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. A theoretical study showed that it is possible to prepare a SnGe mixed metal perovskite material which absorbs the sunlight. In this study, a new type of SnGe mixed metal perovskite solar cells are 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 perovskite (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 2.5% of Ge, the overall efficiency was enhanced to 4.48%. With the Ge content more than 10wt%, 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 non-doped sample SnGe(0). This work provides a platform for further research on lead-free SnGe based perovskite solar cells.

References

Edge Management in Reduced-Dimensional Perovskites Enables Efficient and Stable Light-Emission Lin Quan1,2 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 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.

Perovskites with a Twist—Discovery of the Mixed Valent Double Perovskites CsSnX3 (X = Br, Cl) Kyle M. McCall, Constantinos Stoumpos, Grant C. Alexander, Giancarlo Trimbarchi, Bruce Wessels and Mercouri G. Kanatzidis; Northwestern University, Evanston, Illinois, United States.

The success of halide perovskites as optoelectronic materials has spurred immense interest in these remarkable compounds. The perovskite structure has formula AMX3 and consists of corner-connected MX6 (M2+ a metal cation, X– a halide) octahedra with large A+ cations (Cs+, CH3NH3+, CH(NH2)2+ = FA+) in the voids. This framework is quite flexible, enabling substitution on all three sites to form a variety of compositions. Halide substitution tunes the band gap. Many experimental and theoretical works followed, but it quickly became apparent that only specific pairings of M+ and M3+ form 3D double perovskites with bandgaps below 3 eV. Double perovskites utilizing alkali metals as M+ have long been studied as scintillators, but their bandgaps lie outside the visible spectrum where optoelectronic materials are sought. This narrows the field of M+ to Ag, Cu, Au, Ti, and In, but these have issues of their own. Ti halides are extremely toxic, while Au halides are light sensitive and prefer linear coordination. Cu+ is unstable in octahedral coordination, while In+ reduces both Sb5+ and Bi3+, seemingly leaving Ag+ as the only option. We wondered whether the In+ cation could coexist with In3+ without reducing In3+ and maintain an octahedral perovskite framework. The only inorganic
halides with In⁺ are mixed-valent binaries with non-octahedral In⁺, but we hypothesized that Cs⁺ would be large enough to stabilize the In⁺X₆ octahedron. Accordingly, the solid-state reaction of CsX, InX, and InX₃ yielded the mixed-valent double perovskites CsInX₃ (X = Cl, Br), with bandgaps of 2.20 eV for the bromide and 2.97 eV for CsInCl₃, similar to the Cs₂AgBiX₆ analogues. The CsInX₃ structures have significant disorder at the In⁺ site due to lone pair expression, characterized by large x-ray diffraction thermal parameters. CsInCl₃ in particular can form two structures, one which is a 3D perovskite and another in which an In⁺Cl₆ octahedron rotates 45° to better accommodate the larger In⁺ ion, similar to the case of the mixed valent CsTlCl₃. The phase behavior is studied by synchrotron x-ray diffraction, showing evolution to a cubic structure at high temperature. DFT calculations show indirect band gaps, and as a result there is no photoluminescence at room temperature. The CsInX₃ are a unique addition to the inorganic double perovskites, with CsInBr₃ just the second bromide after Cs₂AgBiBr₆.

SESSION ET05.11: Mechanistic Studies Using Microscopic Imaging and Advanced Materials/Physical Characterization
Session Chairs: Juan-Pablo Correa-Baena and Marina Leite
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room Ballroom B

1:30 PM *ET05.11.01
Strain-Related Defects in Metal Halide Perovskites Samuel D. Stranks; University of Cambridge, Cambridge, United Kingdom.

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 approaches 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.

2:00 PM *ET05.11.02
Perovskite Dynamics from the Nano- to the Macroscale Marina S. Leite; University of Maryland, College Park, Maryland, United States.

To date, the main limitation toward hybrid perovskites’ implementation into commercial light-absorbing and light-emitting devices is this material lack of stability upon exposure to: humidity, oxygen, temperature, light, and bias [1, 2]. Thus, understanding and controlling the driving forces for perovskites’ degradation and the possible pathways for recovery are imperative for the development of reliable devices. We resolve the influence of each abovementioned parameter onto the perovskites’ electrical and optical responses from the nano- to the macroscale. We demonstrate, in real-time, the dynamic open-circuit voltage of perovskite solar cells by novel scanning probe microscopy methods [3, 4], resulting from light-induced ion migration [5].

We determine the effect of chemical composition of the photoluminescence hysteresis of Cs-triple cation perovskites, as a function of humidity cycles [6]. Additionally, we identify a fully reversible voltage response within grains for Cs-triple cations perovskites upon exposure to 1-sun illumination. These measurements show the importance of correlating the local, nanoscale behavior with macroscopic electrical and optical responses. Finally, we will present a machine learning approach to track device performance [1], including a route to prevent material degradation, and to material recovery.


2:30 PM ET05.11.03
Ionic Properties of Twin Domain in Methylammonium Lead Triiodide Yongtao Liu¹, Lian Collins², Anton V. Ievlev³, Alex Belianinov², Stephen Jesse², Scott Retterer², Kai Xiao, Mahshid Ahmadì, Sergei V. Kalinin⁴, Bin Hu⁴ and Olga Ovchinnikova⁵; ¹Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The twin domain in methylammonium lead triiodide (MAPbI₃) has drawn extensive research efforts, starting the discussion on its ferroic nature. Given the coupling of defect chemistry and ionic states with ferroelectricity/ferroelasticty, the research efforts should be extended to its chemical behavior. Our earlier investigations revealed the ion segregation correlating to the ferroelastic domain contrast. To follow up, we systematically investigate the chemical evolution of the ion migration in the MAPbI₃ twin domains in this work. Using Band Excitation Contact Kelvin Probe Force Microscopy (BE-cKPFM), we reveal the absence of ferroelectric polarization switching in this material, as our data indicate an underlying electrochemical effect regarding ion migration. This disproves the ferroelectric origin of the previously observed butterfly and hysteresis loops in Switching Spectroscopy piezoeclectric force microscopy (SS-PFM). In addition, Band Excitation Scanning Kelvin Probe Force Microscopy (BE-sKPFM) measurement, which was utilized to study the electrochemical activities in the twin domain, indicates that the difference in ion migration and/or surface charging effect in the adjacent domains. This result implies a different ionic conductivity and a variation of electronic properties in adjacent domains. Combining Band Excitation PFM (BE-PFM), nanoscale infrared spectroscopy (Nano IR), and scanning probe microscope (SEM), we clarify the correlation between ionic diffusion, electronic
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 Hanifi1, Jon A. Schuller1, Alberto Salleo2 and Michael L. Chabinyc2; 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 (C4H9NH3)2(CH3NH3)3Pb4I13 and (C4H9NH3)2(CH3NH3)3PbI3 on the meso- and nanoscales. 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-incident 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 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 BREAK

3:30 PM ET05.11.05
Hybrid Inorganic-Organic Perovskites—From Film Optical Response to Device Functionality Nikolas Podraza, Biwas Subedi, Kiran Ghimire,
Prakash Upety, Maxwell Junda, Cong Chen, Chongwen Li, Dewei Zhao, Zhaoming 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 MAPbI3 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 structural superlattice are expected to spontaneously and automatically occur in context with situation. The organometal halide perovskite self-adjusts their

4:15 PM ET05.11.07
Strain Effect on Stability and Band Gap in CsPbBr3 Crystal via NanoXRD Xueying Li1, Yanqi 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 ABX3 (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 CsPbBr3 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 CsPbBr3 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 pivotal 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 (MAPbI3) 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 piezoelectric force microscopy (PFM) andKelvin 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. Padture 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 (FAPI3) 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 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

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 Javadi1, 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 extraplateal conductivities ($\sim 10^{-7} \text{ S cm}^{-1}$) and diffusion coefficients ($\sim 10^{-7} \text{ cm}^2 \text{s}^{-1}$) 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 electronic charge pinning or screening effects under external biasing. Unexpectedly, at high forward biases, we found that there is a capacitive 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 capacitive effects coupled with increased ion mobility.

ET05.12.02

Understanding the Solvent Engineering Method Through In Situ Time-Resolved GIWAXS

Rodrigo Szostak1, Paulo E. Marchetti1, Adriano Marques1, Marco S. Medeiros1, Jean C. Silva1, Matheus Holanda1, Hélio N. Tolentino1 and Ana F. Nogueira1, 1University of Campinas, Campinas, Brazil; 2Brazilian Synchrotron Light Laboratory, Campinas, Brazil.

Organic inorganic hybrid perovskites (OHP) is the most promising material to achieve 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 process, 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$_x$FA$_{1-x}$PbBr$_{3}$ 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 XRD peaks emerged attributed to a-phase of the perovskite and intermediates. The intermediates’s 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 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, Wenhai Li, Yuanyuan 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 δ-FAPbI$_3$ phase at room temperature has been a major impediment. The need for prolonged heat-treatments at temperatures $\geq 150$ °C to obtain the desirable α-FAPbI$_3$ phase often leads to film degradation. Heat treatment also produces fine-grained films with high grain-boundary density, which is detrimental to PSC performance and stability. In this context, we have discovered a new phenomenon, where fine-grained (~175 nm) δ-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 films 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. Noel1, Alba Pellarquín2, Federico Pulvirenti2, Henry Snath3, Seth R. Marder1 and Barry P. Rand1; 1Princeton University, Princeton, New Jersey, United States; 2Physics, University of Oxford, Oxford, United Kingdom; 3Chemistry, 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 in 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 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 photovoltic 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. Haroldson1, Artur Ishiev2, Patricia Martinez1, Masoud Alahbakhshi1 and Anvar A. Zakhidov1; 1The University of Texas at Dallas, Richardson, Texas, United States; 2MISIS, Moscow, Russian Federation.

Exciting reports about simple layer cesium halide 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 (~2–0 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 Ripolles1, Esteban Ciment-Pascual1, Javier Bartolomé-Vilchez2, Alicia de Andrés3 and Carmen Coya1; 1ETSIT, Universidad Rey Juan Carlos, Madrid, Spain; 2ETSI Industriales, Universidad Politécnica de Madrid (UPM), Madrid, Spain; 3Facultad de CC Físicas, 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] Conversion efficiencies reaching 22.1%.

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 Pacifi; 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 nanostructure 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 nano-imprint 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 (Cs2AgBiBr6) solar cells using the planar structure are demonstrated. The prepared Cs2AgBiBr6 films are composed of high-quality grains 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 CsPbI3 Thin Films with Large Quasi–Fermi Level Splitting
Pascal Becker1, 2, Jose Marquez Prieto1, Anamr Al-Ashouri1, Charles Hages1, Hannes Hempel1, Justus Just1, Steve Albrecht4 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.
funnelled to the lowest band-gap phases of the materials through an energy transfer process that considerably increases local carrier concentration, leading 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 reconstruction could be expected to lead to 18% efficient inorganic perovskites solar cells.

ET05.12.10 Photodetectors and Solar Cells Using Indium (I) Iodide as Active Material Marina Ustino

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 solar cells fabricated using low-cost solution process. Perovskite solar cells can potentially accomplish a revolution in 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. Bouassis 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 photocarrier (pin)-type solar cells 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 a significant increase in the overall efficiency.
to enhanced photoluminescence quantum efficiencies. Crucially, the geometry, rate and efficiency of this funneling 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 Pb2+ 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/CH3NH3PbI3 Interface in Perovskite Solar Cells from ***Ab Initio*** Molecular Dynamics**  
*Rabi Khanal*, Nicholas Ayers1, Sheila Briggs1, Soumik Banerjee2 and Sanarat Choudhury1; 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 CH3NH3PbI3/phenyl-C61-butyric acid methyl ester (PCBM) interface. The CH3NH3PbI3 is the photocative 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. CH3NH3I vs. PbI2 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**  
*Indrachapa Bandara R M1,2, Imalka Jayawardena1, Andrew Parnell2, Benjamin G. Freestone3, Stephanie Adeyemo3, Hannah Joyce3, Radu Sporea1 and Ravi Silva1; 1Department of Electrical and Electronics Engineering, University of Surrey, Guildford, United Kingdom; 2Department of Physics and Astronomy, The University of Sheffield, Sheffield, United Kingdom; 3Department of Engineering, University of Cambridge, Cambridge, United Kingdom.

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 PVs 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 PVs is the fast oxidation of Sn2+ to Sn4+ which results in 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 SnF2. This process however, while inhibiting the perovskite oxidation, generates Sn4+ ions in the system by the oxidation of Sn2+ to SnF2, which are hardly removed from the system. Interestingly, extraction of Sn4+ 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 Sn4+ 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 (Cs0.05(FACs0.83MA0.17)0.95PbI3Sn0.13). 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 Sn4+ is extracted through toluene enabling a more purified Pb-Sn perovskite absorber layer growth. The extraction of the Sn4+ by toluene is further strengthened by the studies on the C60(FACs0.83MA0.17)0.95PbI3Sn0.13 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-Controlled Synthesis to Self-Assembled Supercrystals with Tunable Optical Properties**  
*Lakshminaryana Polavarapu*1,2; 1Ludwig-Maximilians-Universität München, Munich, Germany; 2Center for NanoScience (CeNS), Munich, Germany.

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-controlled 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 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, nanoparticles (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 supercrys (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, Nasir Venkatesan1, Jon A. Schulier2 and Michael L. Chabinyc1, 2, Materials, University of California, Santa Barbara, Santa Barbara, California, United States; 2Electrical and Computer Engineering, University of California, Santa Barbara, Santa Barbara, California, United States; 3Physics, 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. Through characteristic crystallization 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)2(CH3NH3)4PbI6, Ruddlesden-Popper phases through in situ video, PL and XRD of drop-cast films. Film growth proceeds through a distinct C4H9NH3+-rich solvated structure before forming smaller grains of C2H5NH3+-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 impedes 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 RbnSbCl3 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, Rb21Sb9Cl48. 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 excitation 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 Rb21Sb9X48 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, Tongcai1, Meidian 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 (FAPbX3, 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 FAPbI3 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, FAPbI3 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 FAPbI3 NCs using pressure, but more importantly
Grain boundaries (GBs) are the most prominent microstructural features that play significant roles in determining the physical properties and photovoltaic functions of the halide perovskite (HP) thin films. Herein, we demonstrate several unique chemical approaches to functionalize the HP GBs continuously at the nanoscale. The key to the unprecedented success of the controlled functionalization is the strong molecular interaction between HPs grains and functionalizing agents. Microscopic characterization methods including analytical transmission electron microscopy have been employed to confirm the precisely controlled microstructures in our HP thin films. Combined experimental and theoretical studies have shown that the confocal functionalization of HP GBs not only leads to electronic passivation of defects, but also protects HP grains from moisture/oxygen ingestion and unfavorable phase transformation. As a result, highly efficient and stable perovskite solar cells are demonstrated. The concept of confocal functionalization of the HP GBs is paving the way for developing higher-performance perovskite solar cells of the future.

Organic-inorganic halide perovskite solar cells (PSCs) have drawn a great deal of attention in the photovoltaic research community due to their high efficiency over 22% and simple manufacturing process. A high quality perovskite film is critical to obtain PSCs with both superior performance and high reproducibility, especially when constructing large area polycrystalline films in ambient condition. Motivated by the common wisdom that thicker films are easier to process and therefore offer better controllability in large area production of optoelectronics device when compared with thinner ones. Here, we employ a simple perovskite formation process to fabricate perovskite films with thickness over 1 μm in ambient condition. By careful control of the perovskite component and formation process, the resultant perovskite films exhibit full coverage and excellent crystallinity with low surface roughness and low thickness variation. The high quality of the films is further evidenced by significantly enhanced photoluminescence lifetime, slower charge recombination constant, much lower intrinsic trap density, higher conductivity and much longer carrier diffusion length to achieve the balance of device efficiency and film thickness. These results suggest that we obtain high quality thick perovskite thin films with this simple method. Our resultant mesoscopic PSCs with active area of 0.1 cm² achieve an average power conversion efficiency (PCE) of 19.1% (with small PCE standard deviation) and a stabilized efficiency approaching 19%. Moreover, our 5 cm × 5 cm PSC module device with active size of 12 cm² also deliver a PCE of 15.3%, strongly suggesting that our method is compatible with further upscaling. In addition, the resultant un-encapsulated small size PSCs exhibit an excellent T80 lifetime exceeding 1600 h under continuous light illumination with maximum power point tracking in dry N₂ environment.

Grain-Boundary Functionalization in Halide Perovskites

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

Investigation and Application of Carboxylic Acid Functionalized Perovskite Surfaces

Kenneth Zielinski; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Methylammonium lead iodide perovskites 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.

High Performance Inverted Planar Heterojunction Perovskite Solar Cells with High Open-Circuit Voltages

Deeving Luo1, 2, 3; Qiuhuang Gong1, 2, 3 and Rui Zhu1, 2, 3; 1State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, Department of Physics, Peking University, Beijing, China; 2Collaborative Innovation Center of Extreme Optics, Shanxi University, Shanxi, China; 3Collaborative Innovation Center of Quantum Matter, Beijing, China; 4Collaborative Innovation Center of Extreme Optics, Shanxi University, Shanxi, China.

Inverted planar heterojunction perovskite solar cells (PSCs) have attracted attention because of the low-temperature, versatility of energy-band engineering, and a simplified device structure[1, 2]. However, their low power conversion efficiencies (PCEs) are still inferior to the regular PSCs with a mesoporous TiO₂ structure[3, 4], mainly due to low open-circuit voltages. To address this issue, we demonstrate a solution-processed secondary growth (SSG) technique that could be used to tune the nature of mixed-cation mixed-halide perovskite films. The resulting films exhibit more n-type in nature and establish a wider bandgap layer close to the surface of the perovskite, along with the reduction in unwanted centers. By the use of perovskite film treated with the SSG-G growth, we ultimately achieved a comparable Voc (1.21 V) to regular structure PSCs without compromising the short-circuit current density and fill factor, leading to substantial increases in PCEs for inverted planar heterojunction PSCs[5]. Such high PCEs of 21.51% have been the best result for inverted planar heterojunction PSCs. Our approach will also be broadly applicable to other perovskite-based optoelectronic devices.

References


Inorganic and Organic-Organic Perovskite Solar Cells

Zonghao Liu, Tony K. Lee, and Wei Chen; Brown University, Providence, Rhode Island, United States.

Perovskite solar cells (PSCs) have attracted attention because of the low-temperature, versatility of energy-band engineering, and a simplified device structure[1, 2]. However, their low power conversion efficiencies (PCEs) are still inferior to the regular PSCs with a mesoporous TiO₂ structure[3, 4], mainly due to low open-circuit voltages. To address this issue, we demonstrate a solution-processed secondary growth (SSG) technique that could be used to tune the nature of mixed-cation mixed-halide perovskite films. The resulting films exhibit more n-type in nature and establish a wider bandgap layer close to the surface of the perovskite, along with the reduction in unwanted centers. By the use of perovskite film treated with the SSG-G growth, we ultimately achieved a comparable Voc (1.21 V) to regular structure PSCs without compromising the short-circuit current density and fill factor, leading to substantial increases in PCEs for inverted planar heterojunction PSCs[5]. Such high PCEs of 21.51% have been the best result for inverted planar heterojunction PSCs. Our approach will also be broadly applicable to other perovskite-based optoelectronic devices.

References:

SESSION ET05.13: Nanocrystals and Single-Crystals

Friday Morning, November 30, 2018

Hynes, Level 3, Room Ballroom B

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 CsPbBr₃Cl₂ 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 ultraviolet-sensitive, 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. Further, 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 I_D vs. V_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 graphene with respect of the Dirac point. 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 Cs₄PbBr₆ Yoon-Kwang Jung¹, Ji-Sang Park² and Aron Walsh¹, 2; 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 opto-electronic properties, but recently, they are being studied for light-emitting applications [3]. Beyond regular perovskites based on a corner-sharing octahedral network, Cs₄PbBr₆, which is called as zero-dimensional perovskite, is getting attention because of its highly-efficient green light luminescence [4]. The reported band gap of Cs₄PbBr₆ 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 been 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 Cs₄PbBr₆. We investigate the chemical and physical properties of the Cs₄PbBr₆ 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.

Highly Luminescent Phase-Stable CsPbI₃ Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield

Feng Liu¹, Yiaohong Zhang², Chao Ding¹, Taro Toyoda¹, Shuzi Hayase² and Aswani Yella; Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, India.

Current 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 heterovalent 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 hexagon 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.

9:15 AM ET05.13.06
Understanding the Roles and Developing Strategies to Overcome Shallow Defect Levels in Cesium Lead Halide Colloidal Nanocrystals

Brent A. Koscher¹, ², Joseph Swabek¹, ² and A. P. Alivisatos¹, ²; University of California, Berkeley, Berkeley, California, United States; ²Materials Science, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

An intellectual explosion in the ever-expanding world of nanoscience has led to the development of facile synthetic protocols for a high level of material control at the nanoscale. The culmination of several decades of research has led to the ability to routinely synthesize specific types of cadmium chalcogenide quantum dots with quantum efficiencies exceeding 95%. However, enabled by a facile synthesis and driven forward by excellent optoelectronic properties, the all-inorganic perovskite quantum dots (CsPbX₃; X = Cl, Br, I) have attracted considerable attention among academic researchers for decades. A relatively nascent field. This is a material that performs with up to 90% photoluminescent quantum yield following the synthesis, quite encouraging, but accessing materials with the highest possible quality is crucial to fully realize the potential of the material. This leads to the interesting question: What prevents the quantum efficiency from truly being unity? The same property that enables easy access of the material, namely a low temperature synthesis, also opens the door for a number of very real problems. While it is generally accepted that the lead halide perovskites are positioned with an unusually high defect tolerance, they are not defect impervious, and are particularly susceptible to the pernicious shallow electronic states that result from the lead-rich synthetic conditions and labile surface halides. We have been working to carefully understand the role that the lead-rich surface conditions of CsPbX₃ quantum dots have on the optoelectronic properties of the material, conditions that result in multi-exponential excited state lifetimes and sub-optimal quantum efficiencies. Through careful manipulation of the surface structure we are able to alleviate the deleterious lead-rich surface, changing the hard to describe multi-exponential excited state lifetimes to single-exponential lifetimes typical of two-level systems, an unusual property for a nanocrystal ensemble. For example, through our studies we have found that no more than 50 extra surface leads are responsible for reducing the photoluminescence quantum yield of a CsPbBr₃ nanoparticle to 85%, these lead atoms represent a small but detrimental population of surface lead atoms. A careful manipulation and removal of harmful atoms while maintaining the integrity of the nanoparticle as a whole is crucial in being able to access the highest quality nanomaterials. To this end, tailoring approaches to manage atoms in specific locations or with specific energies is necessary to continue to improve material performance and understand how to best utilize the materials moving forward.

9:30 AM ET05.13.07
Highly Luminescent Phase-Stable CsPbI₃ Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield

Feng Liu¹, Yiaohong Zhang², Chao Ding¹, Taro Toyoda¹, Shuzi Hayase² and Qing Shen¹; ¹The University of Electro-Communications, Tokyo, Japan; ²Kyushu Institute of Technology, Tokyo, Japan.

Perovskite quantum dots (QDs) as a new type of colloidal nanocrystals have gained significant attention for both fundamental research and commercial applications owing to their appealing optoelectronic properties and excellent chemical processability. As a result, a wide range of potential applications, synthesizing colloidal QDs with high crystal quality is of crucial importance. However, like most common QD systems, those reported perovskite QDs still suffer from a certain density of trapping defects, giving rise to detrimental non-radiative recombination centers and thus quenching luminescence. In this work, we developed a triethylphosphine (TOP)-based route which yields phase-stable monodisperse CsPbI₃ QDs with the best-so-far quantum efficiency up to 100%, signifying the achievement of almost complete elimination of the trapping defects. Ultrafast kinetic analysis with time-resolved transient absorption spectroscopy evidences the negligible electron or hole trapping pathways in our QDs, which explains such a high quantum efficiency. Solar cells based on these high-quality perovskite QDs exhibit power conversion efficiency of 9%, showing great promise for practical application.

9:45 AM BREAK
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 phosphoric or phosphonic 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 Gramlich¹,², Bernhard J. Bohn³,², 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; ²Nanosystem 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 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 APbX₃ [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, 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 trion (charged exciton) generation is a major factor lowering PLQYs, the size dependence of trion generation probability is analyzed from the proportion 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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¹ L. Protesescu et al., Nano Lett. 2015, 15, 3692.
² J. A. Castaneda et al., ACS Nano 2016, 10, 8603.

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 Motaharifar¹, Lakshmi N. Murthy¹, Marissa N. Higgins¹, Diego Barrera¹, Troy Daunis¹, Yangzi Zheng¹, Anton Malko¹, Fernando Ely⁴,⁵, Manuel Quevedo-Lopez⁶, Mark Lee⁷ and Julia W. Hsu⁴; ¹Materials Science and Engineering, The University of Texas at Dallas, Richardson, Texas, United States; ²Chemistry, University of Washington, Seattle, Washington, United States; 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 photodetection. 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 electrical contacts on fragile single crystals can be 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 phosphoric or phosphonic 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.

measurements over different spectral ranges, we are able to separate the effects of surface and bulk defects on the recombination dynamics of photo-generated charged carriers. We further apply SPV measurements to obtain the minority carrier (electron) diffusion length for the MAPbBr3 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 FA1-xCsxPb(I1-yBry)3—Temperature Dependence and Impact on Band Gap
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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 FA1-xCsxPb(I1-yBry)3 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 FA1-xCsxPb(I1-yBry)3 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 MAPbI3, 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 FA1-xCsxPb(I1-yBry)3 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 PbSn perovskites, which share the same tetragonal space group [3]. This work establishes a phase diagram that may help interpret photostability 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 CsPbX3 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 CsPbI3 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 thermochromatic 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 CsPbX3 nanostructures with high PLQY throughout the exchange reaction. Via developing a novel localized anion exchange, we demonstrate spatially resolved multi-color CsPbX3 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
Maryna Bodnarchuk1, 2, Simon C. Boehme3, Stephanie ten Brinck1, Caterina Bernasconi2, Yevhen Shylko1, Maksyn V. Kovalenko2, 4 and Ivan Infante1; 1Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; 2ETH Zürich, Zürich, Switzerland; 3Vrije Universiteit Amsterdam, Amsterdam, Netherlands.

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 CsPbBr3 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 ageing 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
1:30 PM ET05.14.01

Hyperbolic Dispersion Arising from Anisotropic Excitons in Two-Dimensional Organic-Inorganic Hybrid Perovskites

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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

Silvia Colella1, 2, Antonella Giuri1, 2, Carola Corcione1, Aurora Rizzo1, Feng Gao1, Michele Saba1, Giovanni Bongiovanni4, Jianwu Wang3 and Andrea Listorti2

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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 cells1 and light emitting diodes,2 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,3 here we explore the use of a tailored biopolymer, starch, as templating agent for the growth of formamidinium (FA)- and methylammonium (MA)-based tri-iodide 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 suitable for different large area deposition techniques), of the perovskite grain size and of the layer thickness, by simply adjusting the polymer:perovskite relative concentration. Our approach was validated by outstanding performances in both light emitting (LED) and photovoltaic (PV) devices with outstanding results. We obtained an inverted, planar, mild temperature processed solar cell with a 17% efficiency and a LED characterized by an EQE of ~5% and, most important, among the highest reported radiances for NIR PeLEDs. (i.e. 206.7 W/sr*m2 obtained at very high currents; about 1000 mA/cm2).


Exciton binding energy than 3D perovskite. However, the complexity in the wet-chemical processes makes the synthesis of high purity homologous 2D perovskites still a big challenge. In addition, the fundamental mechanism of the morphological phase transition and 1D to 2D transition is still lacking. In this direction, we grew a high purity millimeter-sized single crystal 2D RPP (BA$_2$MA$_3$PbBr$_{12.5}$ and BA$_2$MA$_3$PbI$_{12.5}$, n=1, 2, 3) which cover whole visible light range by using slow evaporation at a constant-temperature (SECT) solution growth. Furthermore, due to the pyramid step-like structure, we obtain cavity-free lasing behavior with around 3.7 °C/cm² low 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


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 that carrier recombination is suppressed by forming a high-quality perovskite thin film. The performance of LEDs 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 bimolecular and is characteristic of the 3D regions. From the near-unity PL quantum efficiency and transient kinetics of the emissive layer with/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 50% in the forward direction to indicate the high internal quantum efficiency of the perovskite.

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 Peng You and Feng Yan, Hong Kong Polytechnic University, Hong Kong, China.

We report a cost-effect approach for improving the performance of perovskite solar cells by using novel high-mobility 2-dimensional materials. The surface 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 Hui-Sean King and Andreas Hagfeldt, École Polytechnique Fédérale Lausanne, Lausanne, Switzerland.

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 triiodide and dodecylamines 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 photon excitation, a gradual increase in photoluminescence was observed from the perovskite film, coupled with a minute red-shift. Moreover, the continuous photon excitation, the quantum efficiency (IQE) of the perovskite-based LEDs was 80%, 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.

We 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 Malin B. Johansson1, Ling Xie1, Jakob Thyl1, Tomas Edvinsson1, Mats Göthelid2, Gunnar Niklasson1 and Gerrit Boschloo1; 1Uppsala Universitet, Uppsala, Sweden; 2KTH, Stockholm, Sweden.

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 different dendritic patterns 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. The 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 correlated 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 Philip 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 photocurrent, 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.

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