Halide Perovskites – Optoelectronic and Structural Characterization Methods

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Research into the halide perovskites has exploded over the past decade as their combination of remarkable optoelectronic properties have come to light. As halide perovskite materials come of age, increasing effort is being dedicated to their development into devices, and an in-depth understanding of their physical and functional properties spanning from the atomic to system levels is required. The need for deeper understanding of halide perovskite materials is especially critical because they are currently hampered by their sensitivity to interfacial and bulk decomposition and phase transformation reactions despite their often-ascribed defect tolerance or "self-healing" capabilities. Their sensitivity to perturbations also means that halide perovskites often require special care in characterization of their fundamental and technological properties, precisely because changes in the material are possible under a host of environmental and electromagnetic stressors, including many that are inherent in traditional characterization modalities. This special issue focuses on insights and opportunities in the characterization of perovskites, ranging from recent advances in atomic-resolution microscopy, to new approaches

to assess buried interfaces, to understanding the performance and degradation of perovskite optoelectronic devices via *in situ* probes. The issue combines a mix of progress reports and review articles, as well as practice-oriented tutorials, to bring together the latest understanding of perovskites ascertained from advanced characterization – and in turn to offer best practices and new characterization routes to enable further advances.

The ubiquitous solution processing of perovskites, high ionic mobilities, and their environmental sensitivity leads to significant and at times surprising spatial variations in the compositional makeup of the perovskite itself. Even in determining this most basic aspect of the material, challenges have arisen that require care in the use of ion-, X-ray, and electron-probe characterization. Along these lines, Harvey *et al*. provide an overview of the use of powerful time-of-flight secondary ion mass spectrometry (TOF-SIMS) to understand the three-dimensional distribution of the components in the perovskite film with sub-100 nm spatial resolution in-plane and nanometric resolution in the depth, offering guidance regarding common issues in its application, especially probe-induced artifacts (903674). Kodur, Fenning and colleagues review the use of a range of X-ray microscopies to understand the composition, structure, and functional properties of perovskites, including nano-X-ray fluorescence, nano-diffraction, and X-ray photoemission electron microscopy (903170). Broader studies of perovskites using analytical electron microscopy have been frustrated by the propensity for the electron-beam interaction with the perovskite to degrade the material under investigation. In this regard, Guthrey and Moseley comprehensively review the understanding of defects in perovskites and their degradation reactions ascertained via cathodoluminescence, including analysis of *in situ* electron-beam-induced degradation (903840). Importantly, Ran, Yang, Xiao and colleagues review recent advances in instrumentation, advanced data analysis, and improved understanding of the electron-matter interaction specific to perovskites that have unlocked EM-based nanometric structural and spectroscopic investigations, as well as atomic-resolution imaging (903191). An in-depth discussion of the specific sample preparation and experimental conditions required to produce atomically-resolved imaging of halide perovskites in transmission electron microscopy is provided by Song, Han and colleagues, including advances in cryo-EM applied to halide perovskites (904006).

Investment in careful characterization of perovskite fundamental properties has revealed a unique landscape of light-matter interaction. Underlying the rapid rise of perovskite optoelectronic materials and devices are photophysical properties distinct from those of conventional semiconductors. For example, the exceptional photophysical properties of halide perovskites is evident at ultrafast time scales. Long-lived hot carriers, non-equilibrium carrier dynamics, and charge transport across grain boundary interfaces as analyzed by transient absorption microscopy are reviewed by Deng, Huang and colleagues (903781). In a similar vein, Baranowski and Plochocka review recent efforts to characterize the exciton binding energy in perovskites, identifying carrier-phonon coupling as one root cause of the wide variation of reported values (903659). They show that accounting for polaron effects can substantially resolve the reported discrepancies. More broadly, the practice of, and learnings from, the diverse transient optical spectroscopies applicable to halide perovskites are discussed by Delport, Macpherson, and Stranks (903814). Kirchatz *et al.* provide a comprehensive report on the setup,

experimental conditions, and analysis of photoluminescence spectroscopy, providing rigorous discussion of appropriate modeling and interpretation, which differs depending upon the sample geometry, irradiation intensity and time-dependence (904134). In particular, they provide essential guidance regarding interpretation of both quantitative, steady-state photoluminescence and time-resolved spectroscopy toward understanding the performance potential of perovskite materials and subcells. The ultimate fate of free charge carriers of course also depends on their mobility, which can be effectively analyzed by microwave photoconductive decay as detailed by Savenjie *et al* (903788).

In a landscape of frantic worldwide research into perovskite devices and performance, elucidating the relationships between materials chemistry, synthesis pathway, resulting microstructure and optoelectronic quality and stability is critical. Often, morphologies evident in ubiquitous secondary electron scanning electron microscopy have been used imprecisely to describe the microstructure of halide perovskites. Sun, Adhyaska, and Garnett revisit this record through the use of electron backscatter diffraction (EBSD), analyzing the relationship between the microstructure of halide perovskite films and optoelectronic properties (000364). By mitigating beam damage through the implementation of advanced instrumentation or sample environment in the EBSD characterization, true crystallographic grain orientation and grain boundary characterization is made possible. The detailed structural transformations present during synthesis and degradation reactions in perovskite materials *and devices* are presented by Mundt and Schelhas in their review of *in situ* and *operando* diffraction of halide perovskites (903074). In a complementary description, Babbe and Sutter-Fella review the power of *in situ* UV-Vis and photoluminescence spectroscopies to determine the effect of materials chemistry and synthesis conditions on lateral homogeneity, ion migration, phase separation, and overall degradation (903587).

With often outstanding bulk optoelectronic properties, halide perovskite devices have often been found to be governed by their interfaces. Béchu, Schulz, and colleagues review the application of X-ray, ultraviolet, and inverse photoemission spectroscopies to understanding halide perovskite surface chemistry, band edge positions and band bending, with a particular focus on best practices for performing photoemission spectroscopy when working with the sensitive halide perovskites (904007). Correspondingly, Zhang, Kahn, and colleagues present two guiding case studies on how to avoid issues in the quantification of work function with Kelvin probe force and surface photovoltage microscopy, as well as valence band maxima with ultraviolet photoemission spectroscopy (903252). More broadly, the scanning probe platform presents unique opportunities for near-field optical characterization of perovskites and an understanding of electronic interactions at the nanoscale. Howard, Lahoti, and Leite review recent work in nanoscale mapping of the electronic and chemical properties of perovskites and their evolution over time and under external stressors via SPM techniques including nano-IR spectroscopy and piezo force microscopy (903161).

These surface-sensitive techniques have been applied widely to understand perovskite materials, but an outstanding challenge in the community has been to understand the interfacial structure at the absorber's buried interfaces in functional devices. Toward addressing this knowledge gap,

Xiao, Chen, and colleagues introduce the working principles of interface-sensitive sum-frequency generation spectroscopy and review recent compelling literature results identifying molecular configurations at the interfaces of perovskites and hole- and electron-transport layers (903053).

Finally, detailed optical and electronic characterization of operating devices can provide powerful information about the underlying physics and loss mechanisms. Miyano, Yanagida, and Shirai revisit the broad and often puzzling array of findings from impedance spectroscopy of perovskite devices, highlighting the need to explicitly account for the contributions of mobile ionic species to rationalize impedance data and advocating an interfacial model of an "ionically-gated" transistor (903097). With an eye toward upscaling of perovskite solar cells, Schubert, Glunz, and colleagues examine the progress in using spatially resolved imaging and mapping approaches to identify root causes and local contributions to overall performance loss (904001). Dunfield, Reese, Berry and colleagues provide a thorough examination of limits to stability arising due to the perovskite material itself and its interactions in solar cell devices and modules due to the adjacent layers and operational environment, reviewing efforts to stabilize perovskites and their devices using surface treatments, capping layers, new charge transport layers, and encapsulation (904054). Lastly, with an outlook toward 30% perovskite tandem solar cells, Jŏst, Albrecht, and colleagues comprehensively review progress in the design and realization of perovskite tandem solar cells, with an emphasis on the challenges that remain and the advanced optical and electronic characterization that can guide the field toward this goal (904102).

It is our firm intention that this issue serve as both a useful reference resource for experimentalists and a source of inspiration and new ideas for the community, bringing together the latest advances and discussion of best practices in characterization of halide perovskites under one umbrella. As guest editors, we would like to give our appreciation to the authors for their illustrative contributions, and to the Editors and staff at *Advanced Energy Materials* for their assistance in shaping this Special Issue.

Bio

David P. Fenning is an Associate Professor of NanoEngineering at UC San Diego, where he directs the Solar Energy Innovation Laboratory (SOLEIL). He completed his Ph.D. at MIT in Mechanical Engineering in 2013 investigating high-temperature impurity reactions in silicon photovoltaic materials, followed by an MIT/Battelle postdoctoral fellowship in solar fuels. His current research focuses on elucidating defect and materials chemistry in solar absorbers and catalysts for energy conversion, with a particular emphasis on using *in situ* and *operando* X-ray nanoprobes to gain insights into these energy materials.

Philip Schulz is Research Director at the Centre National de la Recherche Scientifique (CNRS) and pursues his research activities at the Institut Photovoltaïque d'Île-de-France (IPVF), where he leads the Interfaces and Hybrid Materials group installed via a Young Investigator award in the "Make Our Planet Great Again" initiative of the President of the French Republic. Before, he was a postdoctoral researcher at the National Renewable Energy Laboratory (NREL) and Princeton University after having obtained his Ph.D. in physics from RWTH Aachen University, and which included a research stay at the National Institute of Standards and Technology (NIST) through a DAAD scholarship. His research interest focuses on interface design and analysis of new materials for optoelectronic and energy applications with an emphasis on the fields of organic electronics and hybrid solar cells.

Samuel D. Stranks is a University Lecturer in Energy and Royal Society University Research Fellow at the University of Cambridge. He completed his Ph.D. at Oxford University as a Rhodes Scholar followed by a Junior Research Fellowship at Worcester College, Oxford, and a Marie Curie Fellowship at MIT. His group's research focuses on the optical and electronic properties of emerging semiconductors for low-cost, transformative electronics applications including light-harvesting (e.g. photovoltaic) and light-emission (e.g. LED) devices. His group employs optical spectroscopic techniques to understand material and device photophysics on a range of length and time scales, and relates these characteristics to local chemical, structural and morphological properties through multimodal measurements.