

Photophysical Processes in Metal Halide Perovskites

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The irruption of lead halide perovskites (LHPs) into the field of optoelectronics more than a decade ago revolutionized the research in materials for emerging photovoltaic and light emitting technologies. Evidence of this impact was the large number of materials scientists and technologists working, at that time, in small molecule, polymer, quantum dot or dye based optoelectronic devices, just to name a few, that reoriented their interest to focus their efforts on the development of these highly promising newcomers. The field of LHPs greatly benefited from this circumstance, as a wide diversity of knowledge and tools were applied to their development. LHPs, with the general formula ABX_3 ($A \equiv$ a monovalent cation, such as methylammonium, formamidinium, cesium, rubidium or a combination of these; $B \equiv$ a bivalent metallic cation, such as lead or tin; and $X \equiv$ a halide anion, such as chlorine, bromine, iodine or a combination of these), showed extraordinary light harvesting and charge transport properties, and could be easily processed and integrated in solar cells or light emitting diodes (LEDs) in different configurations. As a result of this, the sunlight power conversion efficiency (PCE) values of photovoltaics started skyrocketing very early in the field, displaying a steep slope in the PCE evolution charts. Although with some delay, the performance of perovskite LEDs followed a similar trend. These advances were even more surprising if one considered that LHPs were synthesized and processed at much lower temperatures than their already commercial IV and III–V semiconductor counterparts, which make them considerably more defective. Their astonishing defect tolerance was probably the first of many fascinating fundamental questions that gathered solid-state physicists and chemists around LHPs. In fact, most of the intriguing characteristics of LHPs involve photophysically induced processes, which are the subject of this Special Issue.

Photophysical processes in LHPs have indeed attracted the interest of many experimentalists and theoreticians. Although perovskites can absorb and emit light very efficiently, these properties show an intrinsic instability that arises from their specific defect structure and its high sensitivity to the environment. This is a unique characteristic of LHPs that is not shared by other semiconductors used in optoelectronics. For instance, upon excitation with photons of energy above the electronic bandgap in the presence of molecular oxygen, a layer


of negatively charged oxygen species is formed on the surface of IV or III–V type semiconductors. This has no effect on the bulk properties of these materials: optical absorption, photoluminescence or charge transport all remain unaltered by this interfacial phenomenon. However, photoexcitation in organic LHPs triggers complex activation and degradation processes as a result of the formation of those same oxygen species. Ion migration, defect annihilation, lattice distortion and/or restructuring, and, in the case of mixed halide perovskites, phase segregation are examples of photoinduced effects that occur in LHP. In a sense, this lack of stability is the price one has to pay for having a semiconductor suitable for optoelectronics that can be processed at a lower temperature. Hence, the optoelectronic properties of the LHP semiconductor will depend on the specific synthesis conditions employed, the electric fields it is subjected to, light exposure, the nature of the neighboring layers, the presence of dopants, surface treatments, etc.

The maturity of the field of LHPs is recognized not only in the high values of sunlight PCE or electroluminescence external quantum efficiencies that have been reached in the optimized versions of perovskite solar cells and LEDs, respectively, but also in the profound understanding and control of many of the fundamental photophysical processes that determine the performance and stability of these devices. In this Special Issue, the readers will find excellent examples of the application of deeply analytical tools to understand the mechanisms behind the observations, as well as of the control that results from this analysis to attain materials and devices with enhanced performance and stability. Central to this field, and underlying all research herein reported, is the subject of the relation between defect structure and photoluminescence, which is explicitly dealt with in five works in the Special Issue (2001327, 2001380, 2001969, 2002221, 2100710). Three articles (2001317, 2001786, 2100133) focus on the always-relevant topic of the influence of the environment on such defect structure and how that determines the photophysical response of LHPs. The current and growing interest in nanocrystalline and low-dimensional perovskites is reflected in the high number of manuscripts discussing this topic (2001647, 2001766, 2001875, 2100114, 2100605, 2100620), which cover both fundamental and applied aspects from very different perspectives. Other pertinent specific topics also present in this Special Issue encompass the photon upconversion and downconversion in LHPs (2001470), the intriguing photoinduced processes occurring in the technologically-relevant bulk mixed halides (2001440, 2100635), and the critical issue of standardization of gain measurements (2001773), key for the development of lasers. Finally, two reviews (2002128 and 2002167) and one research article (2100646) deal in great detail with the latest advances in perovskite LED technology.

The works gathered herein exemplify the great interest in understanding and controlling the photophysical processes that occur in LHPs, although it would be impossible to cover all of them in a single thematic issue. Research efforts aim

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 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adom.202101738>.

DOI: 10.1002/adom.202101738

at establishing the cause and the mechanism behind each photophysical response, as well as the effect of each external factor on the optoelectronic performance of perovskites. Success in this endeavor will allow producing devices with enhanced stability and efficiency.

We would like to sincerely thank all our colleagues for their outstanding contributions to this Special Issue in

Advanced Optical Materials, especially during such challenging times (we are truly appreciative of everyone's extra effort to write and review manuscripts during the Covid-19 pandemic). Finally, this issue would not have been consolidated without the immense assistance from Dr. Anja Wecker and her team; thank you for your continued help during the entire process.



Marina S. Leite holds a Ph.D. in Physics and is an Associate Professor at the University of California, Davis. Her research currently focuses on metal halide perovskites for optoelectronics, including the realization of in situ characterization methods to unravel physical and chemical processes from the macro to the nanoscale to enable stable devices, optical materials, and light-matter interactions at the nanoscale.



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