EDITORIAL

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# Emerging Halide Perovskite Materials and Devices for Optoelectronics

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Metal halide perovskites (MHPs) have the general formula $ABX_3$, where A is a monovalent organic or inorganic cation, B is a divalent metal cation (e.g., Pb, Sn), and X is a halide anion. MHPs have been known for over a century, but they have attracted attention and been developed significantly only over the past few years as light-harvesting or light-emitting semiconductors due to superior optical and electrical properties, ease of fabrication, low processing cost, and ease of bandgap tuning. MHPs are promising materials in various optoelectronic and electronic applications such as solar cells, light-emitting devices (LEDs), photodetectors, X-ray detectors, lasers, memory, and artificial synapses. The most active research area considers solar cells and LEDs.

Polycrystalline MHPs possess reasonably high carrier mobility, strong light absoprtion, small exciton-binding energies, and long electron–hole diffusion lengths, which are the key physical parameters that are required to produce high-efficiency solar cells. Due to these key attributes of MPHs, the efficiency of perovskite solar cells has reached 25.2% in the National Renewable Energy Laboratory (NREL) chart. However, these polycrystalline MHP materials for solar cells have a large grain size.

Large grain size causes small exciton-binding energy and long electron–hole diffusion length, so MHPs do not readily generate strong and efficient photoluminescence (PL) and electrolumincence (EL), although they can generate very narrow band emission (full width at half maximum ≈ 20 nm) which can be ideal for high-end panel displays with wide color gamut. Therefore, to fabricate perovskite LEDs (PeLEDs) material engineeering should be used to achieve high efficiencies in PL and EL to overcome these limitations. Such strategies could be used to attempt to spatially confine excitons in nanodimensions, much smaller than the size of the grains in polycrystalline films. Possible strategies include inducing growth of small grains in polycrystalline films, fabrication of quasi-2D material films, and synthesis of nanoparticles. Recently, the external quantum efficiency of PeLEDs that include perovskite nanoparticles has reached 21.3%.

Despite this rapid progress of the efficiencies in solar cells and LEDs that use Pb-based perovskite materials, they have three disadvantages: (1) toxicity of Pb, (2) low stability upon exposure to moisture, light, and thermal stress, and (3) ion-migration-induced degradation of the devices during operation. These problems currently impede commercialization.

Approaches to solve these problems include exploring how to control defects inside cyrstals and on their surfaces, and understanding how ion migration affects the photophysical properties of perovkites materials, as well as the electrical and optoelectric properties and the stability of the devices. This understanding might suggest new crystal structures and guide chemical design of MHP materials, chemical processes to minimize defects, and new architecture designs for device structures. One possible method for a new artchitecture is to use a new functional interlayer to passivate defects and to balance charge-carrier transport and extraction.

Measurements of the electrical characteristics must be performed carefully. Trapped charges and ion migration are responsible for hysteresis and fast degradation in MHP devices, but can induce errors of measurement of the power conversion efficiencies in perovskite solar cells, and of external quantum efficiencies in PeLEDs. Therefore, special care must be taken to reliably and accurately measure the efficiency of perovskite solar cells (as discussed by Xudong Yang, Liyuan Han, and co-workers, article number 1803231). In solar cells, fair assessment can be possible when the devices are certified by NREL or Newport. However, no certification institutions are available for external quantum efficiencies (EQEs) of LEDs, nor have measurement methods and set-ups of EQEs in PeLEDs been standardized. Furthermore most recent high EQEs of ≈20% were measured using a Lambertian assumption without using an integrating sphere or angle-dependent EL data; this approach actually impedes fair assessment of the EQE results in this emerging and competitive PeLED field.

Therefore, this special issue of *Advanced Material* covers various core aspects in fundamentals of MHP materials, their applications to perovskite optoelectronics, and their future challenges, in 13 articles from world-leading experts who are mostly researching solar cells and LEDs.

## Fundamental Physics and Chemistry of MHPs

MHPs have soft, polarizable, and dynamically disordered lattices; these traits lead to slow hot-carrier cooling and the formation of dynamic defects (Xiaoyang Zhu and co-workers, article number 1803054 and Tze Chien Sum and co-workers, article number 1802486). Research on MHP hot-carrier solar cells may drive the efficiency beyond the Shockley–Queisser (SQ) limit. Xiaoyang Zhu and co-workers cover the relationship between the unusual phonon dynamics of MHPs and the

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slow hot-carrier cooling in the low-excitation-density regime. Tze Chien Sum and co-workers (article number 1802486) focus more on the mechanism of slow hot-carrier cooling at high excition density, and discuss the opportunities and challenges of using MHPs with slow hot-carrier cooling to produce high-efficiency hot-carrier solar cells. Annamaria Petrozza and co-workers (article number 1901183) discuss the nature of defects and their photochemistry in MHPs, and suggest how defect activity determines the macroscopic properties of the MHP material and MHP optoelectronic devices. Anlian Pan and co-workers (article number 1806671) explore the physical properties of excitons (e.g., exciton binding energy, exciton dynamics, exciton–photon coupling, exciton–phonon coupling) and of photogenerated charge carriers (e.g., carrier diffusion length, mobility, and recombination) in MHPs.

## Materials Engineering of MHPs

Usually, organic monovalent cations instead of metal cations (e.g., $Cs^+$) are incorpored or combined with metal cations to yield mixed-cation MHPs. However, in principle, organic ions can be incorporated into at least one site (e.g., A, B, or X) in the MHP crystal structure ($ABX_3$) to make organic–inorganic hybrid MHPs or inverse perovskites. Andrew M. Rappe and Julian Gebhardt (article number 1802697) show a variety of combinations of organic ions with inorganic ions to make new types of hybrid MHPs with an $ABX_3$ structure. The existence of these MHPs facilitates the serarch for new MHP materials, and expands their applications into completely new applications beyond optoelectronics.

All of the record efficiencies of perovskite solar cells have been achieved using organic–inorganic hybrid MHPs. However, the instability of organic cations justifies the use of inorganic cations. Futheremore, layered structures can be more stable than the general 3D perovskite structure against moisture and ion migration. In this respect, Lukas Schmidt-Mende and co-workers (article number 1807095) highlight fundamental aspects inorganic and layered MHPs and their applications to optoelectronic and photonic applications.

## Pb-Free MHPs

The MHP solar cells and LEDs with the highest efficiencies have used Pb halide perovskites. However, the toxicity of Pb could impede the implementation of MHP solar cells and LED technologies. Therefore, the Pb content in the MHP materials should be reduced or eliminated by replacing the Pb with less-toxic metal elements. Yanfa Yan and co-workers (article number 1803792) highlight understanding of the electronic, optical, defect, and photovoltaic properties of Pb-free MHPs, in which Pb is replaced by In, Sb, Ge, Sn, and Bi. Mercouri G. Kanatzidis and co-workers (article number 1803230) focus on recent progress in Sn-based perovskite solar cells and discuss the current challenges and future outlook of these devices.

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## Recombination and Defects in Bulk and Interfaces of Optoelectronic Devices

Nonradiative recombination caused by defects (mostly at at grain boundaries and the surface) and heterointerfaces can be a major loss mechanism in perovskite solar cells. The defects also cause significant luminescence quenching in PeLEDs. Therefore, to achieve high efficiency in both solar cells and LEDs, nonradiative recombination must be minimized by interface engineering. Yang Yang and co-workers (article number 1803515) explore various strategies of defect and interface engineering to mitigate nonradiative recombination in perovskite optoeelctronics including solar cells and LEDs. Nam-Gyu Park and Jiangzhao Chen (article number 1803019) explore the origin and characterization of recombination, and then highlight strategies for suppressing trap-assisted nonradiative recombination and interface recombination by focusing on the recombination at the perovskite/electron-transporting layer interface and at the perovkite/hole-transporting layer interfaces in perovskite solar cells.

## Improving External Quantum Efficiency in LEDs

In addition to defect and interface engineering in PeLEDs, engineering MHP materials into different crystal or chemical structures and engineering device architectures to achieve electron–hole balance and to increase light-outcoupling are also important options. R. H. Friend, Felix Deschler and co-workers (article number 1803336) summarize the current understanding of the physics of light-emission in PeLEDs including photon generation and management (e.g., photon recycling to increase outcoupling), and their exploitation in device structures. Tae-Woo Lee and co-workers (article number 1804595) explore the main factors that limit the EQEs in PeLEDs related to the inherent physical properties of MHPs, the morphology of polycrystals and nanocrystals, and the device architectures, and suggest how to overcome the limiting factors to improve the EQE in the material and device apsects.

## Summary

The recent rapid increase in the number of papers produced by this community represents the high attractiveness of these perovskite materials and devices among researchers. I hope that this special issue helps readers to understand the fundamentals of perovskite materials and devices, captures the recent progress of research into perovskite materials, tackles remaining challenges, and suggests solutions that will enable commercialization of perovskite optoelectronic devices such as solar cells, photodetectors, displays, and lighting.

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