

RESEARCH HIGHLIGHTS: Perovskites

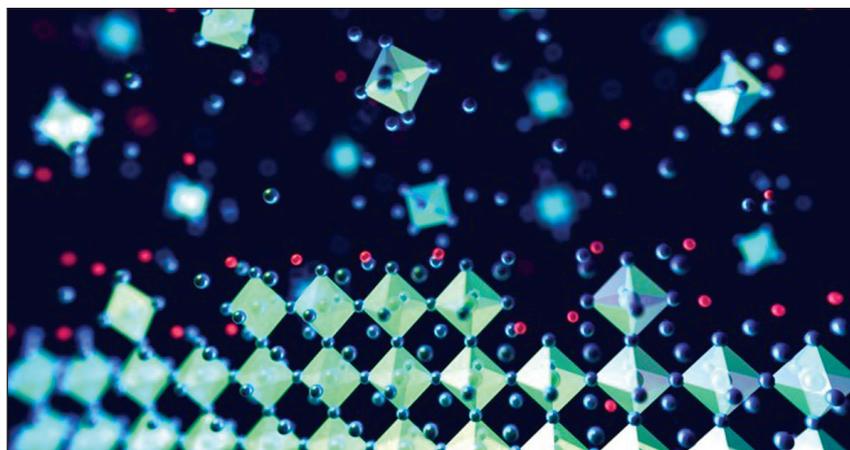
By **Prachi Patel**
Feature Editor: **Pabitra K. Nayak**

Research on perovskites has progressed rapidly, with solar-cell efficiencies now at 22.7%, five times higher than those of the first cells reported in 2009. MRS Bulletin presents the impact of a selection of recent advances in this burgeoning field.

Adding potassium to perovskite films can increase the efficiency of solar cells, shows new research published in *Nature* (doi:10.1038/nature25989).

Perovskite solar cells suffer from nonradiative losses: the recombination of light-generated charge carriers without generating a photon, when carriers get trapped at crystal defects. Efficiency increases when more carriers recombine radiatively, producing a photon that can again generate charge carriers. Another challenge is the movement of ions in the material, which creates spatial distribution of bandgaps and reduces the solar-cell performance.

An international team of researchers led by Samuel Stranks at the University of Cambridge added potassium iodide to a precursor solution for a cesium-formamidinium-methylammonium lead halide perovskite thin film. The potassium iodide forms a layer on the



Atomic-scale view of perovskite crystal formation with added potassium. Credit: Matthew Klug (University of Oxford).

surface and at the grain boundaries of the perovskite, healing the traps and preventing ions from moving.

The films had a very high luminescence yield—important to maximize

efficiency—exceeding 95%, as well as excellent charge transport, with mobilities of more than 40 cm²/V·s. Solar cells made with the films had an efficiency of 21.5%.

The presence of lead in high-performance perovskites raises serious concern. Unfortunately, lead-free perovskites based on tin halide compounds have come up short in terms of efficiency and stability. A new type of three-dimensional (3D) hollow perovskite might be the answer, say Northwestern University researchers.

Mercouri Kanatzidis and his colleagues first reported the hollow hybrid halide perovskites in 2017. They have now used a suite of physical and

spectroscopic methods to study the material's chemical nature and structural properties. Their analysis appears in the *Journal of the American Chemical Society* (doi:10.1021/jacs.8b01034).

Hollow perovskites incorporate the ethylenediammonium (en) cation into 3D ASnX₃ perovskites. Using a range of techniques such as x-ray diffraction, H-NMR (hydrogen-1 nuclear magnetic resonance), and gas pycnometry, researchers confirmed that the en cation creates large vacancies in the metal-halide

framework. Density functional theory calculations showed that this disruption leads to a widening of the material's bandgap, which is important for tandem solar cells in which perovskites sit atop silicon cells. The en cation also makes the material more stable in air and improves its photoelectric properties.

Hollow perovskites present “a new platform of highly promising light absorbers that can be utilized in single junction or tandem solar cells,” the authors say.

Just as for humans, allowing perovskites to soak up sun helps them to relax and makes them more efficient. Constantly illuminating a triple-cation hybrid perovskite thin film expands its crystal lattice, which relaxes strain, researchers report in *Science* (doi: 10.1126/science.aap8671). This, in turn, aligns the material's crystal planes and repairs defects, as well as lowers the

energy barrier at the perovskite-contact interface, improving the material's power-conversion efficiency.

Recent studies have shown that light-induced structural changes play an important role in the optoelectronic properties and stability of devices. But such studies on mixed-cation halide perovskites are lacking. Wanyi Nie, Aditya Mohite, and their colleagues at Los Alamos National

Laboratory illuminated formamidinium-methylammonium cesium lead iodide perovskite thin films using a standard 1-sun source for 180 minutes.

The efficiency of solar cells made with the films went up from 18.5% to 20.5%. Light soaking did not compromise the cells' stability: they worked with minimal degradation for 1500 hours under standard full-spectrum solar illumination.

While halide perovskites are making strides toward commercial devices, their inorganic perovskite oxide counterparts have also attracted attention for solar cells. Devices made from these ferroelectric perovskites are highly stable and have high open-circuit voltages, but they have shown limited efficiencies.

In a *Nature Photonics* (doi:10.1038/s41566-018-0137-0) paper, Canadian researchers demonstrate an alternative route to making high-performance solar cells from perovskite oxides. They made a device from a composite bismuth-manganese-oxide thin film with two different crystal phases—BiMnO₃ and BiMn₂O₅—which had a power-con-

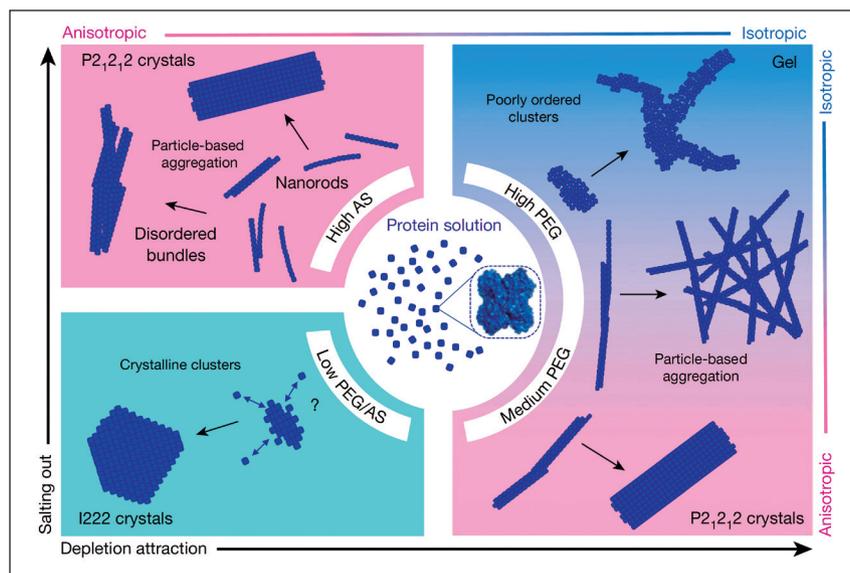
version efficiency of around 4.2%. Inorganic perovskite oxides are ferroelectric. They do not conduct charge carriers well, leading to low photocurrent density and hence low efficiency. But in the mixed material, ferroelectric BiMnO₃ grains are incorporated into semiconducting BiMn₂O₅, which boosts photocurrent density.

Bio Focus

Cryo-transmission electron microscopy reveals protein nucleation pathways

Nucleation is the initial stage of crystallization, a process in which individual building blocks (e.g., atoms and molecules) assemble into various crystalline structures, or "polymorphs." Polymorphs usually exhibit different physicochemical properties due to their diverse structures, and hence are suitable platforms to demonstrate "structure-function" relationships. Therefore, understanding the nucleation and crystallization mechanisms leading to distinct polymorphs is critical. Now, by using cryo-transmission electron microscopy (cryo-TEM), a group of researchers—from the Centre National de la Recherche Scientifique-Université Grenoble Alpes, France; Technische Universiteit Eindhoven, The Netherlands; and the Vrije Universiteit Brussel, Belgium—has directly observed how the protein glucose isomerase nucleates as different polymorphs. Their findings were recently published in *Nature* (doi:10.1038/nature25971).

"One of the most elusive moments to observe the crystallization process is



Schematic illustration depicting the pathways that glucose isomerases take to nucleate into different polymorphs depending on the type and concentration of the nucleation initiators. AS: ammonium sulfate; PEG: poly(ethylene glycol). Both AS and PEG are nucleation initiators. Credit: *Nature*.

the nucleation stage, when a nucleus, or crystalline embryo, is formed," say the authors. To study the nucleation processes of glucose isomerase, they rapidly froze the solutions containing the protein molecules and nucleation initiators at different time intervals during the nucleation. This process stopped the nucleation and allowed

direct imaging of the morphologies of the resultant crystalline structures using state-of-the-art cryo-TEM.

The researchers discovered that the type and the concentration of the nucleation initiators determined the pathways by which the protein molecules nucleated. Twenty seconds after mixing the isomerases with