RESEARCH HIGHLIGHTS: Perovskites

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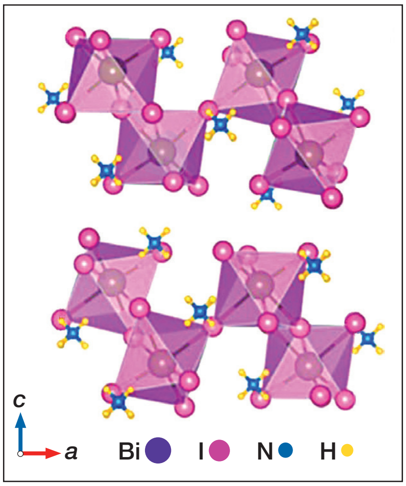
Perovskite solar cells are at the edge of commercial success. New efficiency records are being set at a regular pace, and research on stability and optimization is progressing rapidly. The first commercial products could reach the market by 2020, just a decade since perovskite photovoltaics were discovered. MRS Bulletin *presents the impact of a selection of recent advances in this burgeoning field.*

The same excellent optoelectronic properties that make perovskites promising for solar cells also make them ideal for detecting x-rays and gamma rays. The best perovskite-based x-ray detector is more than 1000 times more sensitive than commercial detectors based on amorphous selenium. However, conventional lead halide perovskites lack stability, and the presence of lead is a concern.

Yang Yang of Zhejiang University in China and his colleagues have made a high-performance x-ray detector using single crystals of the perovskite-like material $(NH_4)_3Bi_2I_9$. The device exhibits a very high x-ray sensitivity of 8.2×10^3 μC Gy_{air}^{-1} cm^{-2} in a parallel configuration, where electricity flows parallel to its crystal surface. The perpendicular direction device, on the other hand, has a very low detection limit of 55 nGy_{air}/s. This is comparable to previously made cesium bromide-based perovskite x-ray detectors and 100 times lower than the 5.5 $\mu Gy_{air}/s$ required for medical diagnostics.

Single crystals of the material are easy to grow in solution at a low temperature, which makes it a promising nontoxic candidate for fabricating large flat-panel x-ray detectors that are low-cost, green, and potentially flexible, the researchers wrote in *Nature Photonics* (doi:10.1038/s41566-019-0466-7).



Crystal structure of $(NH_4)_3Bi_2I_9$. Credit: *Nature Photonics*.

Instability remains the biggest hurdle in the way of perovskites' practical impact. Adding a small amount of fluoride to perovskites can help, researchers have found.

Ion vacancies are a common defect in organic–inorganic halide perovskite crystals that lead to material degradation. They allow anions and cations to migrate to the surface or grain boundaries and trigger reactions that can cause the organic methylamine or formamidine species to escape. Previously, researchers have added halide and other small ions to suppress these defects, but "most strategies focus on passivating or preventing only one type of defect, either the organic cation or the halide anion vacancy," Huanping Zhou of Peking University and his colleagues wrote in a *Nature Energy* (doi:10.1038/s41560-019-0382-6) paper.

The research team decided to use highly reactive fluoride ions. They added a small amount of sodium halide to state-of-the-art cesium formamidinium-methylammonium lead halide perovskites. Solar cells made with the material had a certified power-conversion efficiency of 21.3%. Even without encapsulation, they retained 90% of this efficiency after 1000 hours of simulated sun exposure.

Using density functional theory calculations, the researchers concluded that fluoride ions are effective at suppressing both types of vacancies by forming strong hydrogen bonds with organic cations and strong ionic bonds with lead in the perovskite film.

By using molecular dynamics and density functional theory calculations, researchers have solved the mystery behind a seemingly contradictory property of halide perovskites. Unlike other efficient optoelectronic materials, atoms in perovskites do not oscillate in a well-defined, harmonic way. Such atomic-level disorder does not typically relate to good sunlight absorption.

David A. Egger and Christian Gehrmann from Universität Regensburg analyzed how thermal vibrations in perovskites affect the spatial correlations in the disorder potential for electrons and holes. They found that large nuclear motion in halide perovskites shortened the length at which the disorder occurred. The disorder remained confined to small volumes of the crystal without affecting other crystal domains. The results were published in *Nature Communications* (doi:10.1038/s41467-019-11087-y).

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https://doi.org/10.1557/mrs.2019.212

The light emission lifetime from a family of perovskite-like tin halides depends strongly on temperature, researchers reported in the journal *Nature Materials* (doi:10.1038/s41563-019-0416-2). They used the materials to make a high-resolution remote thermal imaging device.

Thermal imagers are used in medicine, defense, and security cameras and to inspect buildings and pipelines. Conventional devices detect infrared radiation from objects. But another promising approach is to use temperature-sensitive photoluminescent materials that emit visible light. These materials can be integrated into objects as temperature probes. To measure the object's temperature, the material is hit with laser pulses, and then the temperature-dependent photoluminescent decay is measured. These emitters need to be thermally sensitive (less than 0.1°C) over a large temperature range.

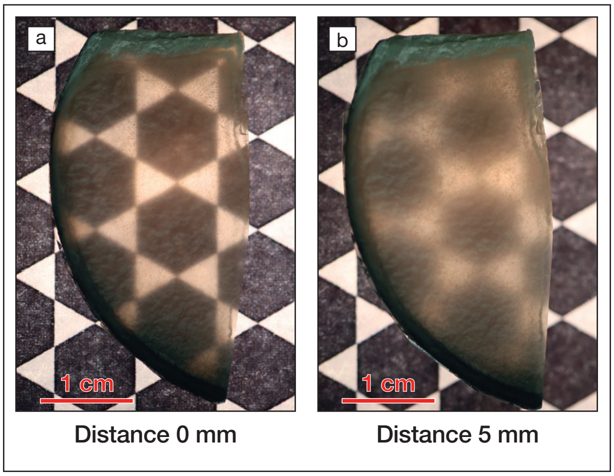
After testing several tin halide perovskite compounds, ETH Zürich's Sergii Yakunin and Maksym V. Kovalenko and their colleagues shortlisted three materials with suitable thermographic properties. The materials could reproducibly measure temperature down to 0.013°C over a range of 100°C. Using low-cost hardware for fluorescence lifetime imaging, the research team was able to use one of the perovskites $(C_4N_2H_{14}I)_4SnI_6$ to make a sensitive, real-time thermal recording.

Nacre-inspired composites display optical transparency, fracture toughness

Inspired by the structure of mother of pearl (nacre), researchers from ETH Zürich have demonstrated an approach to fabricating optically transparent composite materials that are tough, strong, and wear-resistant—normally an elusive combination. As they reported in *Nature Communications* (doi:10.1038/s41467-019-10829-2), the composites have some of the highest strengths among glasses and a fracture toughness up to three times greater than that of common glasses.

Optically transparent materials such as silica- and soda-lime glasses are strong enough to withstand heavy loads, but they are prone to shattering—cracks spread quickly due to their brittle nature. Chemical and thermal treatments can increase the strength of a material but not its resistance to crack propagation, a property associated with fracture toughness. Recently, research has demonstrated that engraving microstructures on a brittle glass surface can increase its fracture toughness, but the microstructures act as defects that reduce the material's strength.

Led by André R. Studart and Florian Bouville (now at Imperial College London), the ETH team took a nature-inspired approach to designing a material that is tough yet strong. The inside of mollusk shells and the outside of pearls are composed of nacre, a strong, tough, iridescent material. This combination of properties is achieved via a two-pronged approach: a chemical composition that offers optical functionality and a complementary microscale architecture that adds toughness to an otherwise brittle material. Studart calls this approach "a pathway to combine, in a single composite material, contradicting properties that would not be achievable using conventional approaches."



Nacre-based composite (59% silica content by volume) that is (a) in contact with and (b) 5 mm above a backlit pattern. Credit: Magrini et al., *Nature Communications*.

Nacre is an inorganic–organic composite with a layered brick-and-mortar structure. Calcium carbonate "bricks" are linked together by thin mineral bridges and surrounded by a "mortar" of biopolymers. Research shows that this design adds toughness to a material, promoting crack bridging, deformation, and other behaviors that slow crack propagation.

To create a similar structure in an optically transparent material, Tommaso Magrini, a graduate student working with Studart, fabricated composites from silica glass flakes and a polymeric mixture of poly(methyl methacrylate) (PMMA) and phenanthrene (PHN) with the same index of refraction as silica. The glass flakes were dispersed in water and slowly settled into horizontally aligned layers. Then the material was dried, uniaxially compacted, and sintered to create bridges at the points where neighboring flakes were in contact. The result was a glass scaffolding of interconnected silica "bricks," similar to the calcium carbonate structure seen in nacre. The polymeric mixture then infiltrated the scaffolding and was polymerized *in situ*.

By exposing the composites to different compressive strengths before sintering, the researchers were able to tune the density of the silica scaffolding. Their characterizations focused on composite samples with 35%, 45%, and 59% silica content by volume.

Mechanical tests showed that composite strength increased with silica content. At 59% silica content, composites displayed the strength of common glasses and transparent polymers. Their surface hardness was an order of magnitude lower than that of silica glass, but at