Blue-green Hf–Zr halide perovskites illuminate path beyond lead

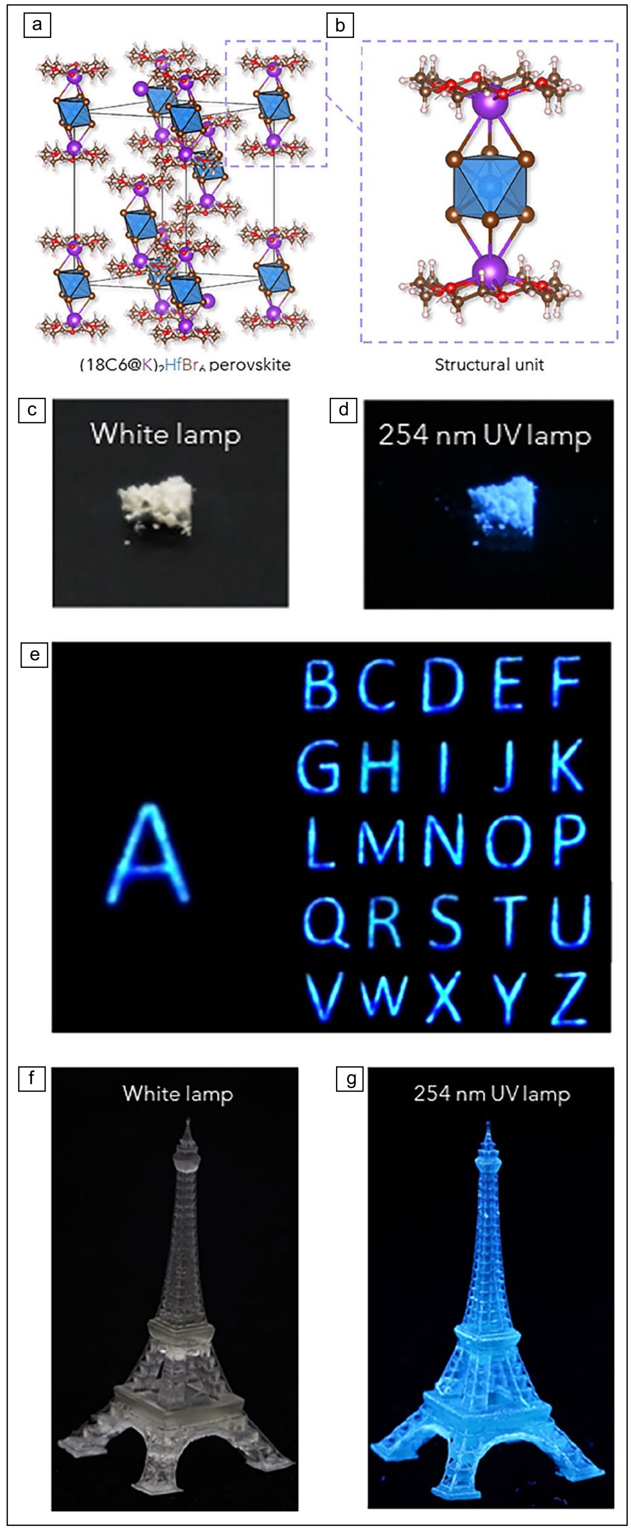
Over the past decade, halide perovskites have emerged as a focal point in the realm of light-emitting materials, owing to their exceptional optoelectronic properties. Although lead-based halide perovskites boast notable optoelectronics properties, their utilization is hindered by the presence of soluble lead and the need for complex colloidal synthesis processes, rendering them unsuitable for large-scale industrial applications. Researchers at the University of California, Berkeley, led by Professor Peidong Yang, have introduced hafnium (Hf) and zirconium (Zr) to replace lead.

In the typical perovskite structure (ABX_3; A = cation, B = divalent metal cation, X = halogen anion), the research team's innovation adopted a structure of A_2MX_6, with the A position occupied by a crown ether containing a cation ($(18C6@K)_2HfBr_6$), M representing the tetravalent cation, and X signifying the halogen anion (see a–b in the Figure, where representative Hf-based perovskites are shown). As reported in a recent issue of *Science* (https://www.science.org/doi/abs/10.1126/science.adi4196), these perovskites were synthesized at a relatively moderate temperature of 80℃. The resulting Hf- and Zr-based materials exhibited blue and green emissions, respectively (see c–d in the Figure), with photoluminescence quantum yields (PLQY) of 96.2% and 82.7 percent. Such high PLQY values hold promise for practical applications.

"A purely speculative question is whether halide photo segregation occurs in these mixed halide systems," says Masaru Kuno, a professor at the University of Notre Dame, who was not involved in this work. "This is a well-known phenomenon of traditional lead-based mixed-halide perovskites. If observed, this would be interesting from a scientific standpoint but detrimental to applications," he says.

"One key challenge is perfecting the synthetic recipe for emitters," says Cheng Zhu, the first author and main investigator of the study, from the University of California, Berkeley. "Despite the straightforward synthesis, identifying the right solvent, concentration, and temperature involves substantial effort and chemistry expertise. Achieving the delicate balance is crucial. After exploration, I found acetonitrile as the sole suitable solvent," he says.

In addition to their purity, this supramolecular approach holds significant potential for solution processability, according to the research team. The $(18C6@K)_2HfBr_6$/polystyrene-dichloromethane ink maintains a PLQY exceeding 90% and is highly processable. Uniform air-stable thin films derived from this ink via drop-casting techniques exhibit blue emission with a PLQY surpassing 80%, making them suitable for patterning, displays, and 3D printing applications (see e–g in the Figure).



Structure and function of $(18C6@K)_2HfBr_6$. (a) The rhombohedral unit cell and (b) the dumbbell-shaped structural unit; (c, d) perovskite powder in white lamp and UV excitation; (e) solution processability and display application; and (f, g) 3D printed Eiffel Tower models under white lamp and UV excitation. Credit: *Science*.

"The use of mixed halide materials mentioned raises concerns about the impact uneven alloying has on color purity given limitations on halide miscibility," Kuno says. "In brief, the materials are still fairly air sensitive. They also undergo photochemical processes upon irradiation that result in their eventual degradation. From the application standpoint, it is worth mentioning that the materials have fairly broad emission linewidths," he adds.

In further studies, Zhu says, "We are researching the potential of our materials for electrically powered lights through electroluminescence. This investigation explores the materials' ability to emit light when subjected to an electric current, crucial for understanding their efficiency in creating light-emitting devices."

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