

Efficient near-infrared luminescence in lanthanide-doped, all-inorganic halide double perovskites

July 21 2022, by Liu Jia



Graphical abstract. Credit: *Angewandte Chemie International Edition* (2022). DOI: 10.1002/anie.202205276

Pb-free all-inorganic halide double perovskites (DPs) have emerged as an important class of environmentally benign phosphors for optoelectronic applications. The studies on them are mainly restricted to the visible spectral region.

Lanthanide (Ln^{3+}) doping is proposed as a valid approach to expand the spectral range of DPs towards the near-infrared (NIR) region. Unfortunately, these Ln^{3+} -doped DPs still suffer from low weak NIR emission of Ln^{3+} due to the small absorption cross-section of Ln^{3+} .

In a study published in Angewandte Chemie International Edition, the



research group led by Prof. Chen Xueyuan from Fujian Institute of Research on the Structure of Matter of the Chinese Academy of Sciences developed a new class of NIR-emitting DPs based on Ln^{3+} -doped Cs₂(Na/Ag)BiCl₆. Benefiting from the Na⁺-induced breakdown of local site symmetry in the Cs₂AgBiCl₆ DPs, efficient NIR emissions of Ln³⁺(e.g. Yb³⁺ and Er³⁺) are realized through Bi³⁺ sensitization.

The researchers first systematically studied the optical properties of Ln^{3+} -doped $Cs_2(Na/Ag)BiCl_6$ phosphors to determine the optimal Na⁺ content, and then comprehensively surveyed the excited-state dynamics and the energy transfer process in the optimal Ln^{3+} -doped $Cs_2Ag_{0.2}Na_{0.8}BiCl_6$ phosphors by means of temperature-dependent steady-state and transient photoluminescent spectroscopy.

Raman spectroscopy analysis and first-principles density functional theory (DFT) calculations confirmed that Na/Ag alloying caused the change of Bi-Cl bond length, which resulted in the local symmetry breaking of Bi^{3+} in $[BiCl_6]^{3-}$ octahedron.

Compared with that of the Na-free $Cs_2AgBiCl_6$ counterparts, the NIR emission of Yb³⁺ and Er³⁺ can be boosted by 7.3-fold and 362.9-fold in $Cs_2Ag_{0.2}Na_{0.8}BiCl_6$ DPs, with the optimal photoluminescence quantum yields (PLQYs) of 19.0% and 4.3%, respectively.

Besides, the researchers employed these Ln^{3+} -doped NIR-emitting $Cs_2Ag_{0.2}Na_{0.8}BiCl_6$ DPs for 365-nm UV-converted NIR Light Emitting Diodes (LEDs), which indicated their potential applications as high-performance optoelectronic devices.

These findings provide new insight into the design of efficient NIR luminescent Ln^{3+} doped all-inorganic halide double <u>perovskites</u> materials, which may accelerate the development of new NIR



optoelectronic devices.

More information: Yifan Pei et al, Boosting Near-Infrared Luminescence of Lanthanide in $Cs_2AgBiCl_6$ Double Perovskites via Breakdown of the Local Site Symmetry, *Angewandte Chemie International Edition* (2022). DOI: 10.1002/anie.202205276

Provided by Chinese Academy of Sciences

Citation: Efficient near-infrared luminescence in lanthanide-doped, all-inorganic halide double perovskites (2022, July 21) retrieved 23 June 2024 from <u>https://phys.org/news/2022-07-efficient-near-infrared-luminescence-lanthanide-doped-all-inorganic.html</u>

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