Researchers unveil local electronic structure of lanthanide-doped double perovskites

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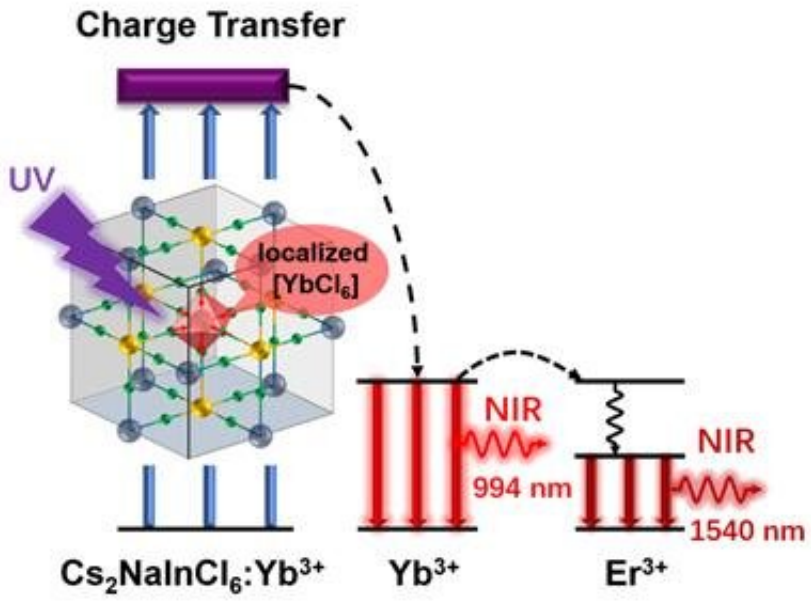

Schematic of electronic structure and luminescence mechanism in $Cs_2NaInCl_6:Ln^{3+}$ double perovskites. Credit: Prof. Chen's group

Lead-free halide double perovskites (DPs) have evoked great interest due to their unique optical properties. Recently, lanthanide ion (Ln^{3+}) with rich electronic energy levels have been proposed for tailoring the optical performance of DPs toward the near-infrared (NIR) regions.

Among these DPs, $Cs_2Na(Ag)InCl_6$ DPs have been widely reported as one of the excellent hosts for Ln^{3+} doping due to their direct bandgap character and high chemical stability. However, their local electronic structures remain essentially untouched, which restricts the development of Ln^{3+}-doped DPs.

In a study published in *Advanced Science*, the research group led by Prof. Chen Xueyuan from Fujian Institute of Research on the Structure of Matter of the Chinese Academy of Sciences introduced Yb^{3+} into $Cs_2NaInCl_6$ DPs and realized efficient NIR luminescence with the optimal photoluminescence quantum yields (PLQY) of 39.4%.

The researchers unveiled the local electronic structure of $Cs_2NaInCl_6:Yb^{3+}$ through density functional theory calculation and Bader charge analysis, which indicated that electrons in $[YbCl_6]^{3-}$ octahedron were strongly localized in $Cs_2NaInCl_6:Yb^{3+}$, while they were delocalized toward Ag^+ in $Cs_2AgInCl_6:Yb^{3+}$. Such a localized electron can effectively boost the NIR luminescence via Cl^--Yb^{3+} charge transfer sensitization in $Cs_2NaInCl_6$.

Benefiting from the localized electrons of $[YbCl_6]^{3-}$ octahedron in $Cs_2NaInCl_6$ DPs, an efficient strategy of Cl^--Yb^{3+} charge transfer sensitization was proposed to obtain intense NIR luminescence of Ln^{3+}.

The researchers demonstrated the proposed novel sensitization strategy for enhancing the NIR emission of Ln^{3+} to be superior to the self-trapped excitons sensitization in the well-established $Cs_2AgInCl_6$ counterparts.

They carried out temperature-dependent steady-state and transient PL spectroscopic measurements to verify the Cl^--Yb^{3+} charge transfer process in $Cs_2NaInCl_6:Yb^{3+}$ by the characteristic transition from charge transfer band (CTB) to $^2F_{7/2}$ (Yb^{3+}) and $^2F_{5/2}$ (Yb^{3+}).

Density functional theory calculation and Bader charge analysis indicated that the $[YbCl_6]^{3-}$ octahedron is strongly localized in $Cs_2NaInCl_6:Yb^{3+}$, which facilitates the Cl^--Yb^{3+} charge transfer process.

Furthermore, the researchers achieved efficient NIR luminescence from Er^{3+} with PLQY of 7.9% in Yb^{3+}/Er^{3+} co-doped $Cs_2NaInCl_6$ DPs due to the energy transfer from Cl^--Yb^{3+} CTB to Er^{3+}.

These findings provide a general approach to achieve effective NIR emission of Ln^{3+} in halide DPs, opening up a new avenue for exploring NIR-emitting perovskite derivatives toward versatile applications.

More information: Siyuan Han et al, Unveiling Local Electronic Structure of Lanthanide-Doped Cs 2 NaInCl 6 Double Perovskites for Realizing Efficient Near-Infrared Luminescence, *Advanced Science* (2022). DOI: 10.1002/advs.202203735

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