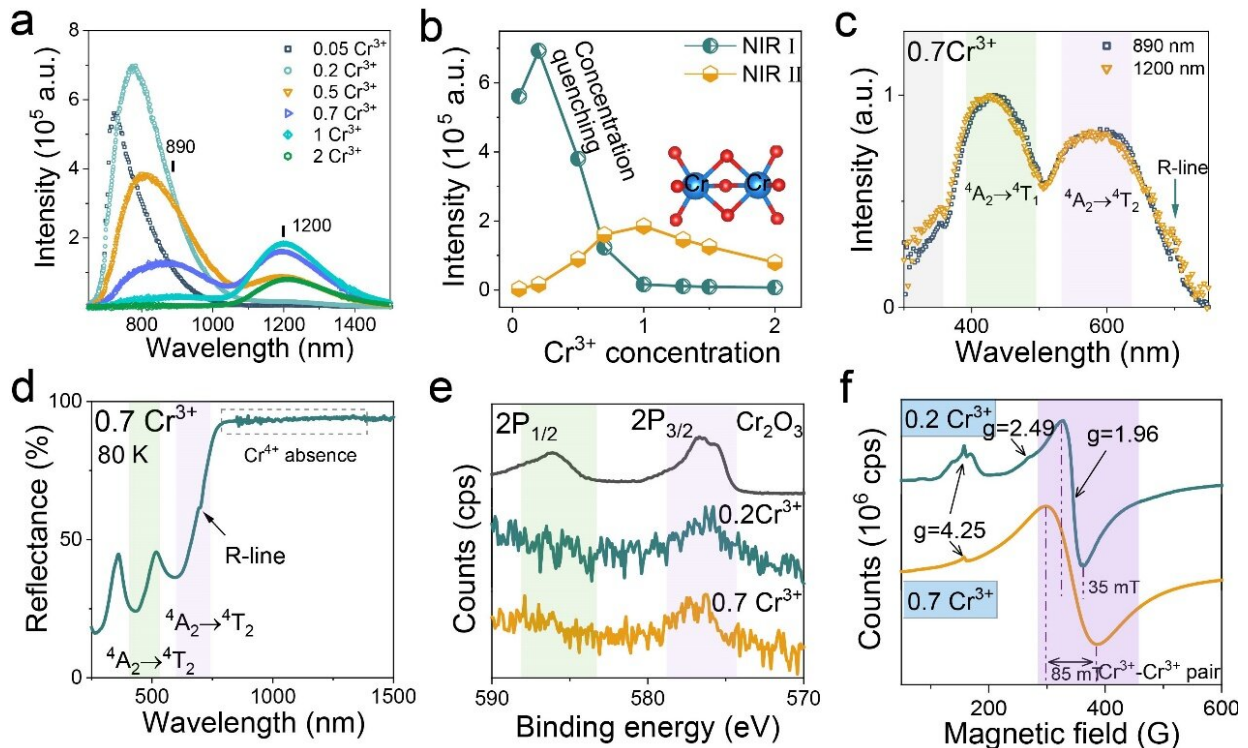


Intervalence charge transfer of Cr³⁺-Cr³⁺ aggregation for NIR-II luminescence

July 26 2023



a, PL spectra of LaMgGa_{11-x}O₁₉:xCr³⁺ (x=0-2) under 440 nm excitation. b, Luminescence intensities of NIR-I and NIR-II versus Cr³⁺ concentration; c, PLE spectra of LaMgGa_{11-x}O₁₉:0.7Cr³⁺ monitoring at 890 and 1200 nm. The excitation signals result from the transitions of isolated Cr³⁺ ion. d, Cryogenic (80 K) UV-Vis-NIR diffuse reflectance curve validating that no absorption of Cr⁴⁺ ion can be traced. e, XPS curves of Cr₂O₃, LaMgGa_{11-x}O₁₉:0.2Cr³⁺, and LaMgGa_{11-x}O₁₉:0.7Cr³⁺ samples validating no chemical shift. f, EPR curves of LaMgGa_{11-x}O₁₉:0.2Cr³⁺ and LaMgGa_{11-x}O₁₉:0.7Cr³⁺ samples. In (f), the broad resonance signal with g of 1.96 is attributed to the Cr³⁺-Cr³⁺ pair, indicating

strong interaction between Cr^{3+} ions. Credit: Shengqiang Liu, Jingxuan Du, Zhen Song, Chonggeng Ma, Quanlin Liu

The near-infrared (NIR) spectrum contains characteristic vibrational absorption bands of numerous organic functional groups. NIR phosphor-converted light-emitting diodes (pc-LEDs) have gathered increasing interests in fields including non-destructive testing and night vision.

In 2016, Osram reported the first NIR pc-LED, SFH4735, while with low output power (16 mW @ 350 mA) and limited wavelengths. Furthermore, luminescent contrast agents operating within the second biological imaging window (1,000–1,800 nm) exhibit lower tissue absorption and scattering coefficients in contrast to the traditional first window (750–950 nm), thereby enabling enhanced detection depth and improved imaging signal-to-noise ratio.

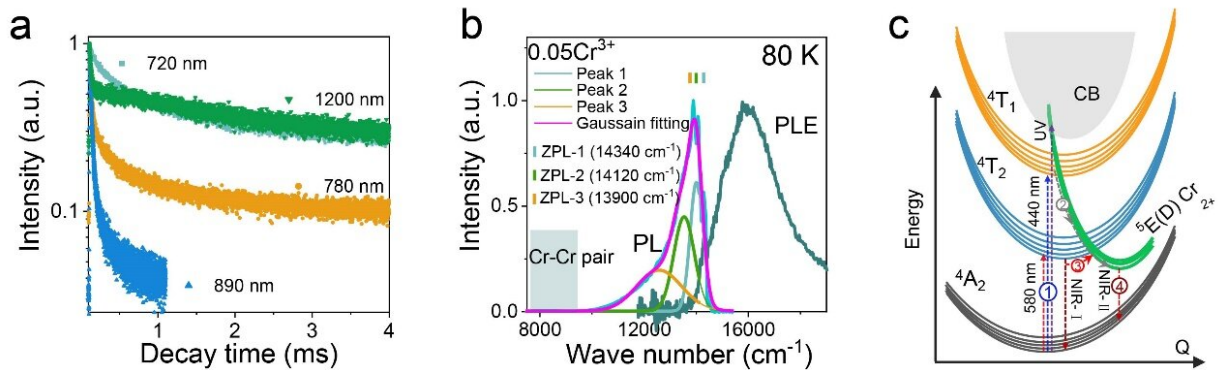
Significantly, the luminescence of Cr^{3+} via engineering the crystal field environment is located in the NIR-I region, as illustrated by the Tanabe-Sugano diagram. The presence of Cr^{4+} ($[\text{Ar}]3d^2$) is capable of extending the emission to the NIR-II region, but the efficiency is subpar due to poor luminescence thermal quenching at room temperature.

In contrast, phosphors doped with lanthanide ions typically exhibit narrow-band multiplets emission, making spectral tuning a challenging task. Hence, it becomes crucial to investigate methods for achieving broadband NIR-II luminescence through ion doping and structural composition.

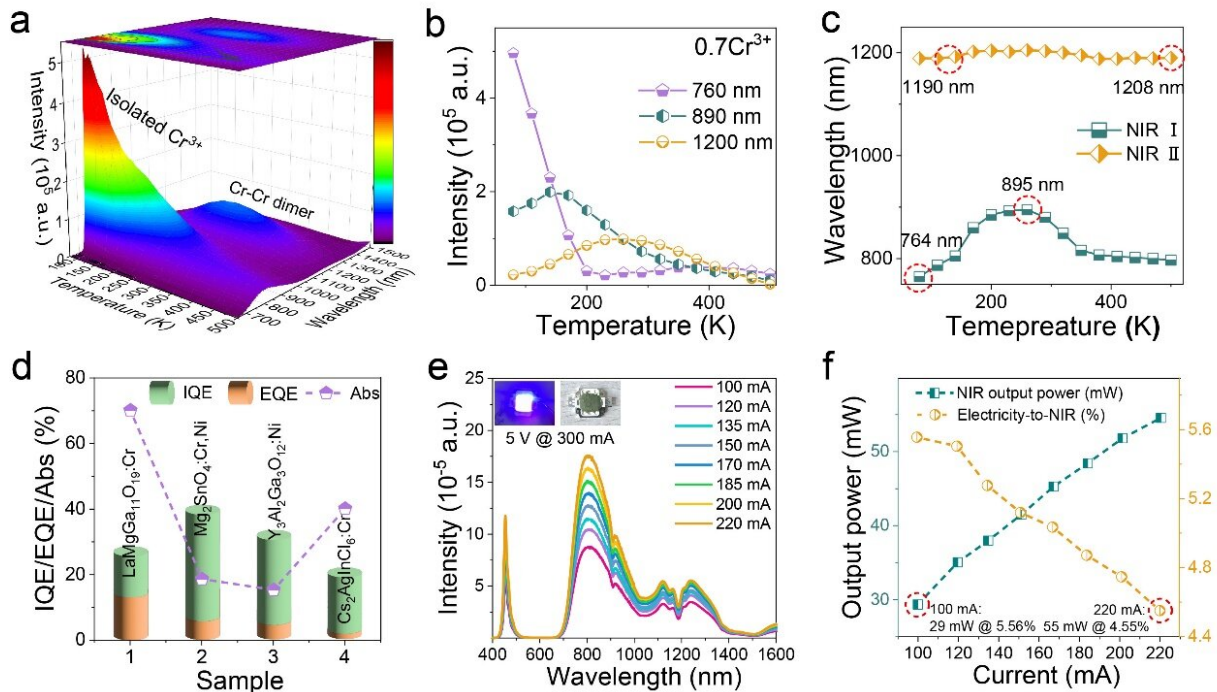
In a new paper published in *Light Science & Application*, a team of researchers, led by Professor Quanlin Liu from School of Materials Sciences and Engineering, University of Science and Technology

Beijing, China, and co-workers have developed the first-ever NIR-II broadband luminescence based on intervalence charge transfer (IVCT) of $\text{Cr}^{3+}\text{-Cr}^{3+} \rightarrow \text{Cr}^{2+}, \text{Cr}^{4+}$ in magentoplumbite-type $\text{LaMgGa}_{11}\text{O}_{19}$.

Based on heavily incorporation of Cr^{3+} ion, $\text{LaMgGa}_{11}\text{O}_{19}$ exhibits dual-emission (NIR-I, 890 nm and NIR-II, 1200 nm) with a full width at half maximum (FWHM) of 626 nm and luminescence external efficiency of 18.9%. They further observed the luminescence anti-thermal quenching behavior (432% @ 290 K vs. @80 K) of target NIR-II luminescence.



a, Cryogenic (80 K) luminescence decay curves of $\text{LaMgGa}_{11}\text{O}_{19}:0.05\text{Cr}^{3+}$ sample monitoring at 720, 780, 890, and 1,200 nm. The luminescence decay lifetime monitoring at 1,200 nm is 2.3 ms, validating the anomalous is not related to Cr^{4+} impurity and magnetic interaction of $\text{Cr}^{3+}\text{-Cr}^{3+}$ pairs. b Magnified cryogenic PL and PLE spectra of $\text{LaMgGa}_{11}\text{O}_{19}:0.05\text{Cr}^{3+}$ sample to estimate the ZPL energies; c Schematic luminescence mechanism based on IVCT. The IVCT between Cr^{3+} centers can be broken down into two separate single-center processes: the oxidation of a Cr^{3+} ion (i.e. $\text{Cr}^{3+} \rightarrow e(\text{VB}) + \text{Cr}^{4+}$) and the reduction of another Cr^{3+} ion (i.e. $\text{Cr}^{3+} + e(\text{VB}) \rightarrow \text{Cr}^{2+}$). The radiative luminescence occurs from the $5E$ ground state of Cr^{2+} ions back to the $4A_2$ ground state of Cr^{3+} . Credit: Shengqiang Liu, Jingxuan Du, Zhen Song, Chonggeng Ma, Quanlin Liu



a, Temperature-dependent luminescence 3D color mapping of $\text{LaMgGa}_{11}\text{O}_{19}:0.7\text{Cr}^{3+}$ sample. b, Luminescence intensities versus temperature monitoring at 760, 890, and 1,200 nm. c, Scatters of peak positions versus temperature. It was observed with anomalous anti-thermal quenching behavior (432% @ 290 K). d, Comparison of IQE, EQE, and Abs values with some reported NIR-II luminescent phosphors. The luminescence IQE and EQE are 27.2% and 18.9%. e, Electroluminescence spectra and photographs of the fabricated NIR pc-LED device by integrating $\text{LaMgGa}_{11}\text{O}_{19}:0.7\text{Cr}^{3+}$ on a commercial 450 nm blue LED. f NIR output power and photoelectric conversion efficiency of the fabricated pc-LED with the tunable driven current. Credit: Shengqiang Liu, Jingxuan Du, Zhen Song, Chonggeng Ma, Quanlin Liu

They observed the NIR-I luminescence at low concentration of Cr^{3+} ions, whereas the NIR-II luminescence appears as the concentration of Cr^{3+} ions increases to 0.5. With a high doping concentration of Cr^{3+} ions, the excitation and absorption signals of Cr^{4+} ions cannot be traced.

Additionally, in contrast to the Cr^{4+} ions, they discovered significantly longer luminescence decay lifetime (2.3 ms) associated with this anomalous NIR-II [luminescence](#). The potential application of $\text{LaMgGa}_{11}\text{O}_{19}:\text{Cr}^{3+}$ phosphor as a light-emitting converter in non-destructive analysis, tissue penetration, and long-distance [night vision](#) is demonstrated via fabricating a NIR pc-LED.

More information: Shengqiang Liu et al, Intervalence charge transfer of Cr^{3+} - Cr^{3+} aggregation for NIR-II luminescence, *Light: Science & Applications* (2023). [DOI: 10.1038/s41377-023-01219-x](https://doi.org/10.1038/s41377-023-01219-x)

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