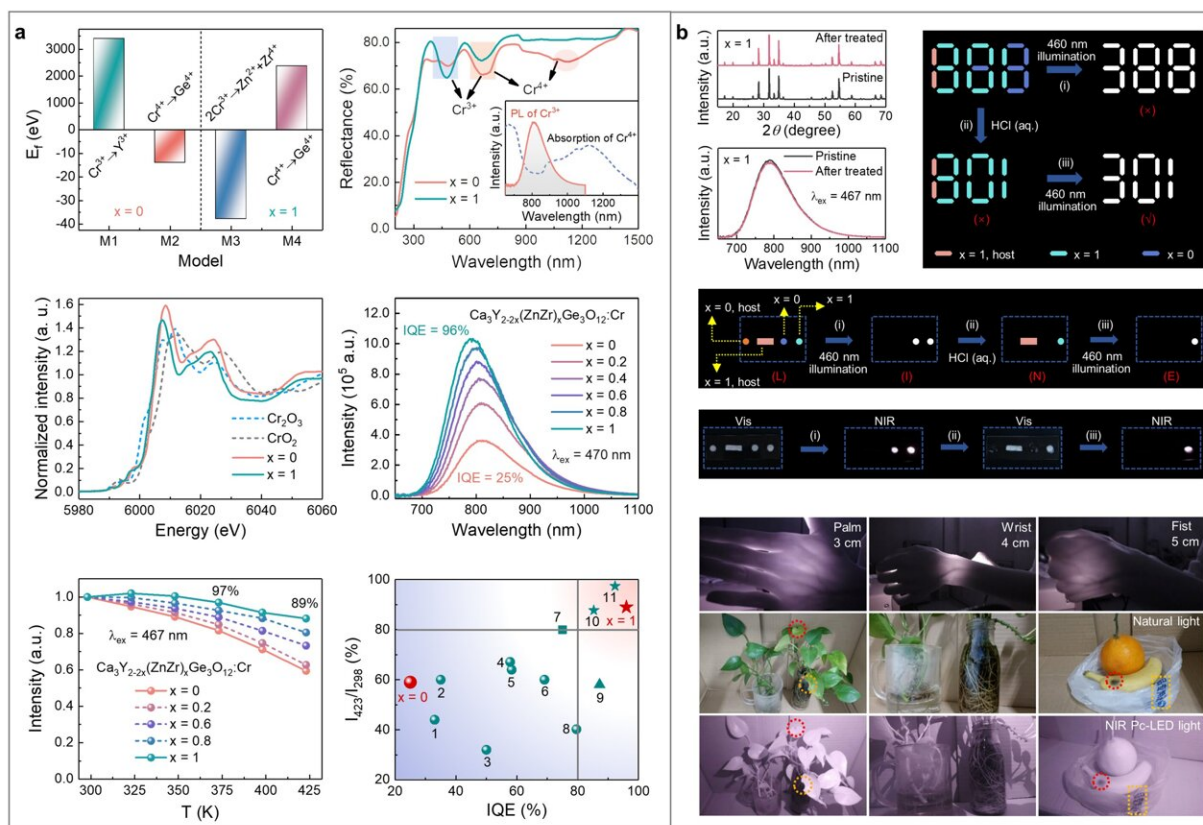


Improving luminescence efficiency and thermal stability of NIR-emitting phosphors

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a, Luminescence optimization of $Ca_3Y_{2-2x}(ZnZr)_xGe_3O_{12}:Cr$ phosphors by cation cosubstitution of $[Zn^{2+}-Zr^{4+}]$ for $[Y^{3+}-Y^{3+}]$ based on valence conversion and site reconstruction. b, Information encryption application and NIR pc-LED applications in bio-tissue imaging, and night-vision. Credit: Dongjie Liu, Guogang Li, Peipei Dang, Qianqian Zhang, Yi Wei, Lei Qiu, Hongzhou Lian, Mengmeng Shang, and Jun Lin

Near-infrared (NIR)-emitting phosphor-converted light-emitting diodes (pc-LEDs) have attracted attention in emerging technology fields such as night-vision and bio-imaging. Currently, the development of NIR-emitting pc-LEDs has encountered a bottleneck due to the lack of blue-light excitable high-performance NIR-emitting phosphor materials.

Although Cr^{3+} -activated phosphors stand out among numerous NIR-emitting phosphors and has recently made progress in realizing tunable broadband emission, major issues still remain their unsatisfactory [luminescence](#) efficiency and poor [thermal stability](#).

$\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ -typed garnets are considered as promising host materials that can address these issues, because their compact coordinated environment and tunable structures may provide diverse luminescence properties including the required ones.

Unfortunately, there is a trade-off between the emission wavelength and efficiency as well as thermal stability. That is, the highly efficient and thermally stable NIR luminescence generally accompanied with short emission wavelength ($^{3+}$ -doped NIR-emitting garnet phosphors).

In a new paper published in *Light: Science & Applications*, a team of scientists, led by Professor Jun Lin from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, and Professor Guogang Li from China University of Geosciences have reported a "kill two birds with one stone" strategy to simultaneously improve luminescence efficiency and thermal stability of the NIR-emitting $\text{Ca}_3\text{Y}_{2-2x}(\text{ZnZr})_x\text{Ge}_3\text{O}_{12}:\text{Cr}$ garnet system by chemical unit co-substitution, accompanied with only slight emission shift.

The developed NIR-emitting phosphors show potential applications in information encryption, bio-tissue imaging, and night-vision. This work provides a new insight for developing high-performance NIR-emitting

[phosphor](#) materials.

To achieve high luminescence efficiency and thermal stability for Cr^{3+} -doped garnet phosphors, two dominant factors should be considered. One is luminescence "killer" Cr^{4+} that shows intensive absorption in NIR region. Another crucial factor is structural rigidity.

In this work, the authors chose $\text{Ca}_3\text{Y}_2\text{Ge}_3\text{O}_{12}$ with a typical garnet structure as an initial host for chromium doping. Through a cation co-substitution of $[\text{Zn}^{2+}-\text{Zr}^{4+}]$ for $[\text{Y}^{3+}-\text{Y}^{3+}]$, a series of $\text{Ca}_3\text{Y}_{2-2x}(\text{ZnZr})_x\text{Ge}_3\text{O}_{12}:\text{Cr}$ NIR-emitting phosphors were synthesized using a traditional high-temperature solid-state method. The underlying luminescence optimization mechanism of this garnet system were investigated.

The [structural analysis](#) and density functional theory (DFT) calculations indicate that chromium ions are very likely to enter the Ge^{4+} sites of $\text{Ca}_3\text{Y}_2\text{Ge}_3\text{O}_{12}$ in the form of tetravalent Cr^{4+} ions. The coexistence of Cr^{3+} and Cr^{4+} is demonstrated to be responsible for the low quantum efficiency of $\text{Ca}_3\text{Y}_2\text{Ge}_3\text{O}_{12}:\text{Cr}$. The designed co-substitution of smaller $[\text{Zn}^{2+}-\text{Zr}^{4+}]$ for $[\text{Y}^{3+}-\text{Y}^{3+}]$ plays an expected role as reductant, which promotes the transformation from Cr^{4+} luminescence killers to beneficial Cr^{3+} emission centers.

This result is also demonstrated by the diffuse reflectance spectra and Cr K-edge X-ray absorption near-edge structure spectra. The valence reduction is related to the successful reconstruction of the octahedral sites for Cr^{3+} ions. Moreover, the introduction of $[\text{Zn}^{2+}-\text{Zr}^{4+}]$ unit also contributes to a rigid crystal structure.

These two aspects together achieve the simultaneous high internal quantum efficiency of 96% and excellent thermal stability of 89% at 423 K, which almost surpasses all of the reported Cr^{3+} -doped garnet

phosphors within similar emission region (770–820 nm). This proves the feasibility of the designed co-substitution in optimizing luminescence properties for Cr^{3+} -doped garnet phosphors.

Furthermore, benefiting from the reconstructed rigid covalent structure, the acid resistance of the phosphor is also greatly improved. Inspired by this, information encryption with "burning after reading" is achieved. Finally, the fabricated NIR-emitting pc-LED shows promising applications in bio-tissue imaging and night-vision.

This work provides a new perspective of luminescence optimization by chemical unit co-substitution, and the revealed universal mechanism could motivate further exploration of high-performance Cr^{3+} -doped NIR-emitting phosphor materials.

More information: Dongjie Liu et al, Valence conversion and site reconstruction in near-infrared-emitting chromium-activated garnet for simultaneous enhancement of quantum efficiency and thermal stability, *Light: Science & Applications* (2023). DOI: [10.1038/s41377-023-01283-3](https://doi.org/10.1038/s41377-023-01283-3)

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