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

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Abstract

The increasing demand for high-contrast biological imaging, non-destructive testing, and infrared night vision can be addressed by the development of high-performance NIR light-emitting materials. Unlike lanthanide (Ln^{3+}) with sharp-line multiplets and isolated Cr^{3+} with NIR-I emission, this study reports the first-ever NIR-II broadband luminescence based on the intervalence charge transfer (IVCT) of Cr^{3+} - Cr^{3+} aggregation in gallate magentoplumbite. In particular, LaMgGa₁₁O₁₉:0.7Cr³⁺ exhibits dual-emission (NIR-I, 890 nm and NIR-II, 1200 nm) with a full width at half maximum (FWHM) of 626 nm under 450 nm blue LED excitation. Moreover, this dual-emission exhibits anti-thermal quenching behavior (432% @ 290 K), attributed to the energy transfer among multiple Cr^{3+} centers. Cryogen absorption spectra, lifetimes decay (2.3 ms), and electron paramagnetic experiments reveal the NIR-II luminescence of the Cr^{3+} - $Cr^{3+} \rightarrow Cr^{2+}$ - Cr^{4+} IVCT transition. The application of LaMgGa₁₁O₁₉:0.7Cr³⁺ in NIR-II biological imaging as an optical contrast agent, non-destructive testing, and night vision is demonstrated. This work provides new insights into broadband NIR-II luminescence under UV-NIR excitation based on the IVCT of Cr^{3+} - Cr^{3+} aggregation.

Introduction

Near-infrared (NIR) luminescence imaging technology, particularly when working in tandem with other modalities to achieve real-time signal acquisition, is a practical tool for in vivo diagnostics and drug delivery^{1–3}. Lightmediated photodynamic (PDT) and photothermal therapies (PTT) are both facilitated through the utilization of the NIR biological imaging window⁴. The research pertaining to luminescence imaging predominantly concentrates on high-performance NIR light-emitting contrast agents that demonstrate excitation and luminescence within the biological imaging window^{5,6}. When contrasted with the conventional first imaging window (NIR-I, 750–950 nm), luminescent contrast agents that operate within the second imaging window (NIR-II, 1000-

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¹Beijing Municipal Key Laboratory of New Energy Materials and Technologies, School of Materials Sciences and Engineering, University of Science and Technology Beijing, Beijing 100083, China 1800 nm) exhibit lower tissue absorption and scattering coefficient. This, in turn, enables a larger probing depth, lower autofluorescence, and a higher imaging signal-to-noise ratio. Besides, NIR phosphor-converted light-emitting diodes (pc-LEDs) are receiving increasing interest in fields such as non-destructive testing, plant cultivation, and night vision^{7,8}. In 2016, Osram reported the first NIR pc-LED, SFH4735, covering 650–1050 nm⁹. However, the output power in the NIR region is typically low in empirical terms (16 mW @ 350 mA), and the luminescence spectrum generally encompasses the NIR-I region with a narrow full width at half maximum (FWHM). Consequently, NIR light-emitting phosphor is the key enabler in integrating this compact NIR device for spectroscopy analysis, particularly within the NIR-II region.

Inorganic NIR light-emitting converters, which consist of lanthanide Ln^{3+} elements, have been extensively studied and reported to be exceptional contrast agents and modulators that utilize linear emission, upconversion, and downconversion¹⁰⁻¹². The distinctive energy-level configuration of Ln^{3+} allows for effortless spectral and temporal discrimination, making it ideal for analyzing

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subcellular processes. However, due to the shielding of *f-f* transition by outer-shell electrons, Ln³⁺ typically exhibits sharp multiplets emissions ranging from ultraviolet to NIR. Consequently, optical contrast agents that relay on Ln³⁺ are inevitably limited by the tunability of the spectrum and may introduce visible background signals. Besides, due to the broadband vibration absorption of organic functional groups^{8,13}, it is unsuitable for nondestructive testing of molecular structures and chemical components. Cr^{3+} ([Ar]3d³) as an ideal NIR light-emitting activator, has been extensively explored in garnet^{14,15}, borophosphate^{16,17}, spinel¹⁸, pyroxene^{19–21}, and doubleperovskite²²⁻²⁴. However, the luminescence of Cr³⁺ in octahedral site is typically located in the NIR-I region, as illustrated by the Tanabe-Sugano diagram²⁵. The presence of Cr^{4+} ([Ar]3d²) is capable of extending the emission to the NIR-II region^{26,27}, but the efficiency of Cr⁴⁺ is typically low due to poor luminescence thermal quenching at room temperature.

Luminescence-molecule aggregation inducing lightemitting was first reported in 1-methyl-1,2,3,4,5-pentaphenylsilole by Tang et al., which provides valuable insight into the anti-quenching behavior of aggregationcaused luminescence^{28,29}. In the case of transition-metal ions (e.g. Mn²⁺, Cr³⁺) doped phosphors, the radiative transition typically originates from an isolated luminescence activator, and luminescence concentration quenching may occur with dopant aggregation³⁰. Our group previously reported the suppressed concentration quenching in Cr^{3+}/Mn^{2+} doped β -Ca₃(PO₄)₂-type compound due to the structural confinement effect^{31,32}. However, due to the significant structural rigidity of β -Ca₃(PO₄)₂, regulating luminescence properties through crystal-field engineering is challenging. In fact, as the concentration of dopants such as Mn²⁺/Cr³⁺ increases, neighboring ions may form dimers or clusters, resulting in strong interactions between the unshielded 3d electrons, such as magnetic interactions and intervalence charge transfer (IVCT)^{33–36}. For NIR spectroscopy applications, we were the first to report the broadband NIR-II emission based on IVCT of Cr³⁺-Cr³⁺ aggregation in gallate magentoplumbite.

The magentoplumbite-type structure with $AB_{12}O_{19}$ formula is commonly found in chondritic meteorites and provides five independent B crystallographic sites (e.g. Mg, Ni, Al, Ga, In) for Cr^{3+} incorporation, which is favorable for achieving tunable NIR-I emission^{37–39}. Due to its long decay lifetime (1.1-2.4 ms) in the $Sr(Al,Ga)_{12}O_{19}:Cr^{3+}$ host, Rajendran et al., attributed the broadband NIR-I emission (740-820 nm) to $Cr^{3+}-Cr^{3+}$ magnetic interaction⁴⁰. In this study, we explore the NIR-II IVCT luminescence (1200 nm) of $Cr^{3+}-Cr^{3+} \rightarrow$ $Cr^{2+}-Cr^{4+}$ in a heavy Cr^{3+} doped LaMgGa₁₁O₁₉ magentoplumbite host. We conducted detailed investigations of the crystal structure, cryogen absorption spectra, lifetime decay, X-ray absorption near-edge structure (XANES), and electron paramagnetic resonance (EPR) experiments to identify the NIR-II luminescence of the IVCT. Notably, LaMgGa₁₁O₁₉:0.7Cr³⁺ exhibits a super-broad dual-emission (890 and 1200 nm) with a FWHM of 626 nm. Besides, this emission presents anti-thermal quenching behavior (432% @ 290 K) due to efficient energy transfer (ET) among multiple luminescence centers. This work offers valuable insights into NIR-II emission based on IVCT of Cr³⁺-Cr³⁺ aggregation, which is capable of high-contrast in vivo imaging and broadband pc-LEDs applications.

Results

Crystal structure and phase identifications

LaMgGa₁₁O₁₉ is crystalized to а hexagonal magentoplumbite-type structure ($P \ 6_3/mmc, 194$) with five independent Ga crystallographic sites, as illustrated in Fig. 1a. The Ga1 2a, Ga4 4 f, and Ga5 12k are six-oxygen coordinated and capable of facilitating the NIR emission of octahedral Cr³⁺ ion³⁷. In particular, Ga4-O octahedra are connected to each other via face-sharing with the shortest Ga-Ga distance of 2.80 Å, while the Ga5-O octahedra share edges with a Ga-Ga distance of 2.94 Å. The Ga1-O octahedra are separated by the Ga3 site, resulting in the longest Ga-Ga distance of 5.81 Å, as depicted in Fig. 1b. Consequently, strong interactions are expected to occur with increasing Cr³⁺ concentration in the Ga4 site, and the Cr^{3+} - Cr^{3+} aggregation may result in pair luminescence due to the short cation distance. Ga3 4 f site is coordinated with four oxygen, while the Ga2 4e deviates from trigonal bipyramidal symmetry and splits into two mirror-symmetric pseudo-tetrahedra. According to our previous work³⁷, Mg^{2+} selectively occupies the Ga1 and Ga3 sites along the (001) plane. Figure 1c illustrates the XRD patterns of LaMgGa_{11-x}O₁₉:xCr³⁺, and all the peaks are indexed to a standard card #JCPDS84-0889, indicating successful incorporation of Cr³⁺ into the hexagonal matrix. As the Cr³⁺ concentration increases, the diffraction peaks slightly shift to higher angels with lattice shrinkage (Fig. 1d), which is attributed to the substitution of smaller Cr^{3+} (0.615 Å, CN = 6) for Ga^{3+} (0.62 Å, CN = 6). The structural refinement pattern (Fig. 1e) indicates that Cr³⁺ selectively substitutes the Ga4 and Ga5 crystallographic sites with 20% and 11% occupations, respectively, while only 5% occupies the Ga1 site (Table S1). Furthermore, the bond valence sum (BVS) of the Ga4 (+2.97) and Ga5 (+3.11) sites are both within +3, whereas the Ga1 site is under-bonded with a BVS value of +3.35, which is significantly larger than +3. This suggests that Cr^{3+} is incorporated into the hexagonal lattice by first occupying the Ga4 and Ga5 sites, which brings the BVS value closer to +3. These findings further indicate



that cation aggregation may occur in the Ga4 site due to the selective occupation of Cr³⁺. Figure S1 displays the microscopic morphology images with an average size of 3 μ m, and the EDS elemental mappings reveal a uniform component distribution.

NIR-II luminescence properties

Figure 2a demonstrates the PL spectra of LaMgGa11- $_{x}O_{19}$: xCr^{3+} at room temperature. Under excitation at 440 nm, the $0.2Cr^{3+}$ sample exhibits a proficient broadband NIR-I emission spanning from 650 to 1000 nm, which is attributed to the ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ spin-allowed transition of isolated Cr^{3+37} . With an increase in Cr^{3+} concentration, the intensity of NIR-I luminescence continuously decreases due to concentration quenching (Fig. 2b). Furthermore, these emission peaks exhibit continuous red-shift from 720 to 890 nm due to the efficient ET among multiple isolated Cr³⁺ centers. The detailed discussion of this phenomenon can be found in the supplementary information and Figs. $S2-S4^{37}$. In addition to the NIR-I emission, a broadband NIR-II emission (1200 nm) emerges with heavy Cr³⁺ incorporation (>0.5). The Cr^{3+} concentration shows little effect on NIR-II emission peaks, but the emission intensity first increases and then quenches. Notably, at 0.7 Cr^{3+} , LaMgGa11O19 displays a dual-emission (890 and 1200 nm) with a FWHM of 626 nm. Furthermore, a broadband excitation ranging from 300 to 750 nm is presented by monitoring these two emissions (Fig. 2c), which are attributed to the ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ and ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ spinallowed transitions of the isolated Cr³⁺. Compared with the NIR-I, the NIR-II emission features a much larger Stokes shift (622 nm), indicating a lower secondary inner filter effect, as shown in Fig. S5. Additionally, there is no overlap between excitation and emission spectra of NIR-II luminescence, indicating high imaging contrast and detection sensitivity, which can be utilized as optical contrast agents. Although the ${}^{3}A_{2} \rightarrow {}^{3}T_{2}$ interconfigurational transition of Cr4+ also presents tunable broadband NIR-II emission, the excitation signal of Cr⁴⁺ cannot be observed monitoring at 1200 nm, validating that the NIR-II emission is unrelated to Cr⁴⁺ impurity. The normalized Cr-K edge XANES of 0.7 Cr³⁺ sample was presented in Fig. S6. Both LaMgGa₁₁O₁₉:0.7Cr³⁺ and Cr₂O₃ exhibit a prominent peak at 6007.1 eV, accompanied by two sub-peaks at 6009.8 and 6022.1 eV. The close agreement with standard Cr₂O₃ suggests that chromium is predominantly presented in the +3 oxidation state. Furthermore, Cr⁴⁺ ions generally exhibit a high degree of tetrahedral coordination stabilization, enabling



f EPR curves of LaMgGa₁₁O₁₉:0.2Cr³⁺ and LaMgGa₁₁O₁₉:0.7Cr³⁺ samples

the dipole-allowed transition of $1 \text{ s} \rightarrow 3 \text{d}$ due to the mixing within the 3d and 4p states. However, the observed low intensity of the pre-edge feature at 5990.2 eV, associated with the $1 \text{ s} \rightarrow 3 \text{d}$ transition, indicates that chromium selectively occupies the octahedral sites, where the $1 \text{ s} \rightarrow 3 \text{d}$ transition is only quadrupole-allowed. Hence, the NIR-II emission is not related to Cr⁴⁺ impurities in tetrahedral sites. Additionally, the broad shoulder observed below 5980 eV can be attributed to the EXAFS signal originating from the La-L2 edge. Furthermore, the crvogenic (80 K) UV-Vis-NIR diffuse reflectance spectra show enhanced Cr³⁺ absorption, but no absorption signals of Cr^{4+} can be traced, as shown in Fig. 2d. Figures S7 and 2e comparatively illustrate the X-ray Photoelectron Spectroscopy (XPS) survey scan and high-resolution Cr 2p spectra, using Cr₂O₃ as the reference. The sharp line with a binding energy of 285 eV (C 1 s related) results from the adventitious hydrocarbons on the surface of the sample, while other peaks can be well indexed to core levels of constituent elements. As the concentration of Cr³⁺ increases to 0.7, the XPS profiles of Cr 2p doublets become almost consistent with the Cr2O3 reference without chemical shift, indicating no modification in the valence state of the host lattice. The dominance of NIR-II emission at higher Cr^{3+} concentration is generally associated with the Cr^{3+} - Cr^{3+} aggregation (i.e. pairs and clusters). The EPR experiments (Fig. 2f) further suggest strong interaction among Cr^{3+} ions in the host lattice. The resonance signal at the low magnetic field region with g value of 4.25 is attributed to the isolated Cr^{3+} in the octahedral sites, while the resonance signal at g = 2.49 is ascribed to the large separation between the two Kramers' doublets of $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$. The resonance signal at the high magnetic field region with g value of 1.96 is attributed to the coupling of Cr^{3+} - Cr^{3+} pairs^{41,42}. The broadening of this resonance profile at high field with increasing Cr^{3+} concentration indicates an enhanced interaction among Cr^{3+} ions.

In contrast to isolated dopants, the anomalous luminescence properties resulting from dopant aggregation are typically explained by magnetic interaction and IVCT. For Cr^{3+} in a strong crystal field environment, the first excited state is ²E, and the spin-forbidden emission (${}^{2}E \rightarrow {}^{4}A_{2}$) of the isolated center and Cr^{3+} . Cr^{3+} magnetic coupling can be spectrally resolved due to these sharp-line features⁴³. Besides, the spin selection rule can be relaxed, leading to a much shorter lifetime, as observed in LaAlO₃:Cr^{3+43,44}. However,



LaMgGa₁₁O₁₉:Cr³⁺ exhibits broadband NIR emission, indicating a weak crystal field environment of Cr³⁺. Energy values E(S) associated with the spin interaction between two activators A and B can be approximately determined by the following equation⁴³:

$$E(S) = -J[S(S+1) - S_A(S_A+1) - S_B(S_B+1)]$$

where *J* is the spin coupling strength parameter, S_A and S_B are the spin quantum numbers of activators A and B, and *S* is the total spin quantum number. Therefore, the value of *E*(*S*) significantly depends on *S* and *J*. In a weak crystal field environment, the ground and first excited states of Cr^{3+} - Cr^{3+} magnetic coupling are $[{}^{4}A_{2}(F), {}^{4}A_{2}(F)]$ and $[{}^{4}A_{2}(F), {}^{4}T_{2}(F)]$. Thus, the total spin quantum number *S* can be obtained through $(S_A + S_B), ..., (S_A - S_B)$, i.e. S = 3, 2, 1, 0. Considering that the coupling parameter *J* is generally within tens of wavenumbers⁴³, the maximum E(S) is approximately 450 cm⁻¹. Similarly, the maximum value of E(S) under a strong crystal field environment is approximately 150 cm⁻¹. However, for the 0.7Cr³⁺ sample, the energy difference between the maximum of NIR-I and

NIR-II emissions is 3715 cm^{-1} . Therefore, the NIR-II luminescence cannot be attributed to the magnetic interaction of $\text{Cr}^{3+}\text{-}\text{Cr}^{3+}$ pair. In fact, the ${}^{4}\text{T}_{2} \rightarrow {}^{4}\text{A}_{2}$ broadband emission of isolated Cr^{3+} and $[{}^{4}\text{A}_{2}(\text{F}), {}^{4}\text{T}_{2}(\text{F})] \rightarrow [{}^{4}\text{A}_{2}(\text{F}), {}^{4}\text{A}_{2}(\text{F})]$ of magnetic interaction cannot be spectrally resolved due to the small value of *E(S)*, which results in a significant spectral overlap.

Luminescence decay lifetimes

The metal-to-metal IVCT state is advantageous in regulating absorption, emission, and non-radiative transition because it is intertwined among the configuration levels of isolated optical-active centers. As Cr^{3+} - Cr^{3+} aggregation increases, electron transfer from one Cr^{3+} ion to its neighbor becomes possible, resulting in the formation of Cr^{4+} and Cr^{2+} pair, e.g. $Cr^{3+}-Cr^{3+} \rightarrow Cr^{2+}-Cr^{4+}$. If radiative recombination follows, the spontaneous emission typically exhibits a large Stokesshift, as seen in the PL spectrum in Fig. S5. Luminescence decay curves further support this assumption, as demonstrated in Fig. 3a, which comparatively presents

luminescence lifetime decay curves at 80 K. All the decay curves can be well fitted by bi-exponential functions⁴⁵:

$$I = A_1 \exp\left(\frac{t}{\tau_1}\right) + A_2 \exp\left(\frac{t}{\tau_2}\right) \tag{1}$$

where *I* denotes the luminescence intensity, τ_1 and τ_2 refer to the decay lifetimes of the first and second exponential fitting, A_1 and A_2 are the exponential fitting constants of τ_1 and τ_2 . In this case, the average lifetime values can be obtained using the following equation:

$$\tau_{average} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} = f_1 \tau_1 + f_2 \tau_2 \tag{2}$$

where f_1 and f_2 denote the percentages of τ_1 and τ_2 components. Bi-exponential fitting results are presented in Fig. S8. Accordingly, the average decay lifetime monitoring at 720 nm is 1.47 ms, attributed to the spinforbidden ${}^{2}E \rightarrow {}^{4}A_{2}$ transition and associated overtones. Monitoring at 780 nm broadband emission, the decay lifetime of 541 μ s is longer than that of other Cr³⁺ doped compounds in the weak crystal field environment. We attribute this to the strong coupling between the ²E and ${}^{4}T_{2}$ configurations. Figure 3b presents the PLE and PL spectra to determine the zero-phonon line (ZPL) energies, which are determined by the intersection of PLE and PL spectra. The energy gap between the sharp R-line (698 nm) and ZPL is only within a few hundred wavenumbers, indicating a strong coupling between the 2 E and 4 T₂ configurations. Monitoring at 890 nm, the lifetime is only 89 µs, indicating a weak crystal field environment. In summary, the luminescence decay curves monitoring at NIR-I emission indicate multiple isolated Cr³⁺ centers with different crystal field environment, consistent with the PL spectra. However, the luminescence lifetime monitoring at 1200 nm is 2.3 ms, much longer than that monitoring at NIR-I emission. Moreover, this decay lifetime is significantly longer than typical Cr^{4+} , which is only a few tens of microseconds^{46,47}. This further confirms that the NIR-II emission is unrelated to Cr⁴⁺ impurity. In general, the spontaneous radiation of the Cr^{3+} *d-d* parity-forbidden transition is relaxed due to the mixing in the $3d^3$ state with other opposite parity. Thus, the emission is partially electric dipole allowed. The spontaneous radiative lifetime τ_{IF} from the initial state *I* to final excited state *F* versus radiative wavelength $\lambda_{\rm IF}$ can be written as⁴⁸:

$$\Gamma_{IF} = \frac{1}{\tau_{IF}} = \frac{64\pi^4}{3h\lambda_{IF}} \chi |\overrightarrow{\mu_{IF}}|^2 \tag{3}$$

where Γ_{IF} denotes the spontaneous radiative rate, *h* is Planck's constant, and $\vec{\mu}_{\text{IF}}$ is the dipole moment between

I and *F*. Therefore, the decay lifetime τ is proportional to λ^3 . After emission wavelength correction, the luminescence lifetimes monitoring at NIR-II emission are still longer than those monitoring at NIR-I emission, as listed in Table S2. For magnetic interaction, luminescence lifetimes generally shorten in Cr3+ and Mn2+ doped compounds, depending greatly on the exchange-coupling parameter $I^{43,44}$. However, for the IVCT pair emission, luminescence decay lifetime is longer than that of the isolated activator^{49,50}. The IVCT transition of $Cr^{3+}-Cr^{3+}$ \rightarrow Cr²⁺-Cr⁴⁺ occurs with a configurational transition between two neighboring Cr³⁺, potentially with low absorption probability compared to the ${}^{4}T_{2} \rightarrow {}^{4}A_{2}$ interconfigurational transition. Accordingly, the luminescence lifetime is longer. Furthermore, isolated Cr³⁺ exhibits multiple excited-state quenching process, for example energy transfer among Cr^{3+} , re-absorption. However, the IVCT luminescence exhibits much larger stokes-shift, with no overlap observed between PL and PLE spectra. Accordingly, the energy transfer and re-absorption process are effectively inhibited, which also possibly leads to the longer luminescence lifetime. Thus, the anomalous NIR-II emission with a large Stokes-shift originates from the IVCT transition $(Cr^{3+}-Cr^{3+} \rightarrow Cr^{2+}-Cr^{4+})$ rather than the magnetic interaction. However, the direct excitation signal of the IVCT cannot be discerned from the UV-vis-NIR diffuse reflection and PLE spectra. Our speculation is that the IVCT transition of $Cr^{3+}-Cr^{3+}\rightarrow$ Cr²⁺-Cr⁴⁺ involves a charge transfer transition between two neighboring Cr³⁺ centers, resulting in a lower absorption probability compared to the stronger ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ intra-configurational transition of isolated Cr³⁺ ions. Consequently, the excitation intensity of the IVCT band is significantly reduced. Furthermore, the IVCT excitation is typically located in the UV region or even at higher energy levels, making it challenging to differentiate due to its overlap with the excitation transitions of ${}^{4}A_{2} \rightarrow {}^{4}T_{2}(F)$, ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$, the O²⁻→Cr³⁺ charge transfer, interband absorption, etc. Furthermore, despite the intervalence charge transfer of $Cr^{3+}-Cr^{3+} \rightarrow$ $Cr^{2+}-Cr^{4+}$ leads to the partial oxidation and reduction of Cr^{3+} . However, the charge transfer transition happens instantaneously, and the XANES, XPS, EPR, and PLE characterizations are steady-state test methods at a macroscopic level. Consequently, the signal associated with Cr^{4+}/Cr^{2+} are challenging to be observed.

Figure 3c constructs a configuration coordinate diagram to explain the IVCT-based NIR-II luminescent mechanism. Firstly, the electron is photo-pumped to the excited states of isolated Cr^{3+} under UV-NIR excitation (①), followed by de-excitation to ${}^{4}T_{2}(F)$ state (②) to produce the NIR-I emission. The IVCT excited state can be understood as the result of the electron transfer between a pair of Cr^{3+} ions, leading to the formation of the product



of two ground states involving Cr^{2+} and Cr^{4+} ions (2). In simpler terms, the transition occurring between these two centers can be broken down into two separate singlecenter processes: the oxidation of a Cr³⁺ ion and the reduction of another Cr³⁺ ion. Following the standard practice on the formation energies of different charge states⁵¹, we can determine the energy position of the ground ${}^{4}A_{2}$ state of the Cr³⁺ ion relative to the top of the valence band by considering the energy change before and after the oxidation reaction $Cr^{3+} \rightarrow e(VB) + Cr^{4+}$, where e(VB) represents an electron located on the top of the valence band. Similarly, we can define the energy position of the ground state ${}^{5}E$ of the Cr^{2+} ion for description of the reduction reaction $Cr^{3+} + e(VB) \rightarrow Cr^{2+}$. Therefore, the energy difference between the ground states of the Cr³⁺ and Cr²⁺ ions provides a clear estimation of the IVCT energy, indicating that the related IVCT emission undoubtedly occurs between these two states rather than involving the ground state of the Cr⁴⁺ ion. It is clear that the condition for the occurrence of IVCT emission is that the ⁵E ground state of the Cr²⁺ ion is situated below the first excited state ${}^{4}T_{2}$ of the Cr^{3+} ion. The energy position of the ⁴T₂ state with respect to the top of the valence band

can be evaluated by adding the energy position of the ground ${}^{4}A_{2}$ state of the Cr^{3+} ion to the transition energy from the ${}^{4}A_{2}$ to ${}^{4}T_{2}$ states of the Cr^{3+} ion. A similar transition process can be observed in the case of a pair of Bi²⁺ and Bi⁴⁺ ions, leading to two Bi³⁺ ions, as depicted in Fig. 2 of the reference⁴⁹. However, due to the lack of spectral data on Cr^{2+} , it is challenging to determine the energy level of Cr^{2+} in the LaMgGa₁₁O₁₉ host.

Time-resolved emissions (TRES) color mapping is further shown in Fig. 3d to identify the ET process among multiple Cr^{3+} centers. With increasing decay time, the emission intensity at 890 nm first increases and then quenches. Additionally, the emission peaks continuously shift toward longer wavelengths (Figs. 3e and f), indicating an efficient ET process among multiple Cr^{3+} centers. In addition to the NIR-I emission, the NIR-II emission also exhibits an efficient ET process due to the initial increase in luminescence intensity, as demonstrated in Fig. 3e and S9.

Luminescence thermal stability and efficiency

Figure 4a illustrates temperature-dependent luminescence 3D color mapping. The integrated intensity decreases continuously with increasing temperature from 80 to 500 K, due to the enhancement of nonradiative transition probabilities, as shown in Fig. S10. At 500 K, the integrated intensity is only ~15.6% of that at 80 K. However, the emission intensities monitored at 890 and 1200 nm exhibit anti-thermal quenching behavior, which means that they first increase and then guench above 140 and 290 K, respectively, as depicted in Fig. 4b. Notably, the luminescence intensity of 1200 nm is approximately 4.3 times higher than that at 80 K. In addition, the NIR-I emission displays a significant red-shift from 764 to 895 nm (Fig. 4c), indicating an efficient ET process among multiple Cr³⁺ centers. The structural analysis reveals that the Ga4 site has the longest Ga-O bond length (Table S3), which is responsible for the 890 nm broadband emission. Moreoever, Ga4-O octahedra are connected by face-sharing with the shortest Ga-Ga distance, enabling 1200 nm luminescence of $Cr^{3+}-Cr^{3+} \rightarrow Cr^{2+}-Cr^{4+}$. As the temperature increases, ET from Ga1/Ga5 to Ga4 site intensifies, leading to the experimentally observed anti-thermal quenching behavior. Additionally, with thermal assistance (3, Fig. 3c), partial electrons selectively transfer from ${}^{4}T_{2}(F)$ to the IVCT state. As a result, the luminescence intensity monitored at 890 nm decreases above 140 K, whereas that at 1200 nm continues to increase by 4.32 times until 290 K.

Reporting of the luminescence internal/external quantum efficiency (IQE/EQE) in the NIR-II region has been scare due to the limited experimental setup. Cr^{4+} and Ni²⁺ are considered as ideal NIR-II broadband lightemitting centers, but they exhibit low luminescence efficiency, for instance, 9.8% EQE for NIR-I to NIR-II emission of Mg₂SnO₄:Ni²⁺⁵², and 8.2% EQE for NIR-II emission of Y₃Al₂Ga₃O₁₂:Ni²⁺⁵³. On the other hand, for the 0.7 Cr^{3+} sample, the IQE of NIR luminescence is estimated to be 27.2% under 440 nm excitation, as illustrated in Fig. 4d. Due to the high absorption rate (69.7%) resulting from the heavy Cr^{3+} incorporation, the EQE is up to 18.9% higher than the above mentioned values. However, the IQE and EQE values of anomalous NIR-II luminescence are only 14.0% and 9.7%.

LED fabrications and applications

To enable practical applications in photo-converted broadband NIR light source, LaMgGa₁₁O₁₉:0.7Cr³⁺ dualemitting phosphor was integrated onto a commercially available blue-emitting chip (450 nm) to fabricate the NIR pc-LED device. Figure 4e shows the electroluminescence spectra with tunable driven current from 100 to 220 mA. The electroluminescence spectra are different from the PL spectra. This is ascribed to the different optical detector, i.e. charge coupled device (CCD) for electroluminescence spectra while photomultiplier tube (PMT) for PL spectra. As the driven current increases, the luminescence intensity continuously grows, and the NIR output power increases from 29 to 55 mW (Fig. 4f). However, the electricity-to-NIR conversion efficiency continuously decreases due to the "efficiency droop" of the blueemitting chip and the luminescence thermal quenching of phosphor. Notably, the NIR output power and electricityto-NIR conversion efficiency under 100 mA driven current are 29 mW and 5.56%, respectively.

Broadband NIR spectroscopy provides massive information about the molecular structures and chemical compositions of organic compounds, making it a favorable method for non-destructive analysis. Figure 5a displays the luminescence spectra before and after penetrating water, absoand alcohol. oil using lute the dual-emitting LaMgGa₁₁O₁₉:Cr³⁺ phosphor. The luminescence attenuations after penetrating these substances are quite different due to their distinct absorption responses toward the NIR region. Alcohol and oil exhibit significant absorptions around 1200 and 1400 nm, which are attributed to the second overtone of the C-H stretching vibration and the first overtone of the O-H stretching vibration. In contrast, water exhibits absorption around 980, 1200, and 1370 nm, which are attributed to the characteristic overtones of O-H stretch. These absorption responses indicate the potential application of this broadband dual-emitting phosphor in non-destructive analysis of agriculture.

Moreover, the NIR-II region features low tissue absorption and scattering coefficients, resulting in a large probing depth and low autofluorescence. Tissue-penetration experiments were further implemented using this NIR pc-LED as a light source, and a 645 nm filter was used to screen out the blue light. Figure 5b illustrates the luminescence spectra and brightness images after penetrating beef tissue. Although the luminescence intensity continuously decreases with increasing tissue thickness, a bright image can be perceived after penetrating 10 mm of tissue. In comparison with living tissue, blood and arteries exhibit much larger absorption coefficients to NIR radiation, enabling efficient vessel localization for infusion application. Additionally, compared with the widely reported angiography based on NIR light-emitting phosphors penetrating living tissue (e.g. human palm), angiography based on light reflection from the tissue surface requires less input power and light loss. Figure 5c depicts the conceptual angiography experiment using this NIR pc-LED as a light source based on light reflection. The result indicates that the black-and-white image of the human arm can be clearly perceived, revealing the internal vascular distribution through shadow dendrites. In contrast, it's difficult to distinguish the artery under indoor lighting.

Furthermore, the naked eyes exhibit low sensitivity to NIR radiation, enabling the use of NIR-emitting phosphors for night vision applications. However, compact NIR pc-LEDs generally exhibit low light output and large light divergence, making them incapable of long-distance



night vision and tracing. Therefore, easy-handled beam homogenizer and condenser systems containing two convex lenses were constructed to obtain convergent NIR light, as schematically shown in Fig. 5d. The convergence distance can be effectively adjusted by altering the distance between the LED and the lens 1. Figure 5e displays the photography of a car with an ordinary camera under indoor lighting at a distance of 5 meters. The object can be directly captured but not in the dark. In contrast, with the aid of the fabricated NIR light-emitting devices, a clear black-and-white photography of the car can be captured under the NIR camera, as shown in Fig. 5f.

Conclusion

In conclusion, this study reports the first-ever broadband NIR-II luminescence based on $Cr^{3+}-Cr^{3+}$ aggregation in magentoplumbite-type LaMgGa₁₁O₁₉. Heavy Cr^{3+} incorporation results in dual-emitting NIR luminescence (890 and 1200 nm) with an FWHM of 626 nm and EQE of 18.9% upon 440 nm excitation. Moreover, this dualemission exhibits anti-thermal quenching behavior (432% @ 290 K), attributed to the energy transfer among multiple Cr^{3+} centers. Cryogenic diffuse reflectance, XPS, EPR, XANES, and luminescence lifetimes validate that the NIR-II emission is unrelated to Cr^{4+} impurity and magnetic exchange coupling but is due to the IVCT of Cr^{3+} . $Cr^{3+} \rightarrow Cr^{2+}-Cr^{4+}$ between neighboring $Cr^{3+}-Cr^{3+}$ pairs. Furthermore, the potential application in non-destructive analysis, tissue penetration, and long-distance night vision using LaMgGa₁₁O₁₉: Cr^{3+} as a photo-converted NIR lightemitting source is demonstrated. This work provides new insights into Cr^{3+} luminescence and opens up new strategies for efficient broadband NIR-II luminescent phosphors based on the $Cr^{3+}-Cr^{3+}$ aggregation.

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Author contributions

Q.L.L., C.G.M. and Z.S. initiated and guided the research. S.Q.L. and J.X.D. performed the experiments. All authors assisted in the editing of the final paper.

Conflict of interest

The authors declare no competing interests.

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