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Highly efficient and thermally stable far-red-emitting phosphors for plant-growth lighting

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ABSTRACT

Far-red phosphor-converted light-emitting diodes (pc-LEDs) are potential efficient and cost-effective light sources for regulating the photomorphogenesis of plants, but it still lacks ideal far-red phosphors with right excitation and emission bands, high quantum efficiency and high thermal stability. Here, we developed an excellent far-red phosphor $Gd_3Al_2Ga_3O_{12}:Cr^{3+}$ (GAGG: Cr^{3+}). Upon blue light excitation, GAGG: Cr^{3+} exhibits efficient far-red emission peaking at 720 nm with internal quantum efficiency as high as 94.1% and zero thermal quenching even at 150 °C. Moreover, a high-performance pc-LED device was fabricated by using the optimized GAGG: Cr^{3+} as the color converter, which can radiate 61.03 mW far-red light at 100 mA with a record photoelectric conversion efficiency of 20.6%. The results indicate that GAGG: Cr^{3+} holds great promise for plant-growth lighting and other LED applications.

1. Introduction

Light is essential to the plants during their whole life from seed germination to flowering and fruiting [1-3]. Generally, three kinds of light in different spectral regions, blue (~440 nm), deep red (~660) and far red (\sim 730 nm), are absorbed by the plant pigments, chlorophylls, the inactive and active states of phytochrome (labelled as $P_{\rm R}$ and $P_{\rm FR}$), respectively [4–6]. For example, blue light absorbed by the chlorophylls can be used for photosynthesis; P_{FR} and P_R can be transformed to each other by absorbing far-red light, which mainly affects the photomorphogenesis and the blooming time of plants [7-11]. Therefore, accurate lighting with particular spectrum is beneficial to the promotion of plant growth. Compared with the well-known incandescent and fluorescent lamps, phosphor-converted light-emitting diodes (pc-LEDs) are undergoing increased attention because of their large flexibility in spectral control as well as their long lifetime, high efficiency and environmental friendliness [12-15]. Since pc-LED devices are fabricated by the combination of blue LED chips and phosphors, their device performances are largely dominated by the luminescence properties of the associated

phosphors. Besides, the generated heat due to the light conversion from blue to far-red is higher than that from blue to green/yellow, which may lead to a strong thermal quenching of the far-red phosphors [16]. Thus, developing far-red phosphors with high quantum efficiency (QE) and excellent thermal stability is full of importance.

Transition metal ions Mn^{4+} and Cr^{3+} are typical activators for far-red phosphors. Mn^{4+} doped phosphors, such as $Ca_{14}(GaAl)_{10}Zn_6O_{35}$: Mn^{4+} [17], $La(MgTi)_{1/2}O_3$: Mn^{4+} [18], $SrLaAlO_4$: Mn^{4+} [19], $LaAlO_3$: Mn^{4+} [20] and $BaLaMgNbO_6$: Mn^{4+} [21] (see Table S1 in Supporting Information), possess low internal QE (IQE) and poor thermal stability. Compared with Mn^{4+} , Cr^{3+} doped phosphors obtain increased attention due to the characteristic emissions in far red and near-infrared regions (for example, Na_3AlF_6 : Cr^{3+} [14], $Gd_3Sc_2Ga_3O_{12}$: Cr^{3+} [16], $YAl_3(BO_3)_4$: Cr^{3+} [22] and $Ca_2LuHf_2Al_3O_{12}$: Cr^{3+} [23], $Na_3In_2Li_3F_{12}$: Cr^{3+} [24], $Lu_2CaMg_2Si_3O_{12}$: Cr^{3+} [25]), but seldom of them (see Table S1) simultaneously possess suitable excitation and emission bands, high IQE as well as good thermal stability, and thus they still can not meet the demand for far-red pc-LED devices.

In this work, Gd₃Al₂Ga₃O₁₂ (GAGG): Cr³⁺ far-red phosphors with

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Fig. 1. (a) XRD patterns of GAGG: $x \operatorname{Cr}^{3+} (x = 0.01, 0.04, 0.08)$. The patterns in the range of $31.8-32.8^{\circ}$ are magnified and shown on the right; (b) XRD refinements of GAGG; (c) Crystal structure of GAGG and its cation coordination environment; (d) HRTEM images of GAGG: $0.08 \operatorname{Cr}^{3+}$; (e) Morphology and elemental distributions of GAGG: $0.08 \operatorname{Cr}^{3+}$; (e) Morphology and elemental distributions of GAGG: $0.08 \operatorname{Cr}^{3+}$; (f) the scalebar is 250 nm).

high QE and good thermal stability were prepared by high-temperature solid state reaction method. We demonstrate that GAGG: Cr^{3+} possesses a high internal QE (IQE) of 94.1%, and the emission intensity at 150 °C shows zero thermal quenching. Moreover, a far-red LED device with 61.03 mW far-red light at 100 mA and a far-red photoelectric conversion efficiency as high as 20.6% is achieved by combing the as-synthetized phosphor with 460 nm LED chip.

2. Experimental section

2.1. Synthesis

Far-red phosphors GAGG: Cr^{3+} were fabricated by the traditional high-temperature solid state reaction methods. The stoichiometric amounts of Gd_2O_3 (99.99%), Al_2O_3 (99.9%), Ga_2O_3 (99.99%), and Cr_2O_3 (99.99%) were used as starting materials and 3 wt% of H_3BO_3 (99.9%) was also added as the flux. The starting materials were weighed and ground in an agate mortar for 40 min. The resulting mixtures were heated in air at 1400 °C for 6 h. The sintering process for two times was carried out with intermediate regrinding. Finally, the products were cooled to room temperature and reground again for the further characterizations. Far-red pc-LEDs were fabricated by coating the mixture of GAGG: 0.08 Cr^{3+} phosphor and transparent silicone on 460 nm LED chip (SMD 5730 PCB), where the mass ratio of GAGG: 0.08 Cr^{3+} to silicone was 1:2.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were obtained on X-ray diffractometer (Rigaku (Ultima-IV)) in the 20 range from 10° to 80° with Cu K α radiation. The counting time was set at 0.12 s with a step size

of 0.02° for each step. Structure refinement was carried out by the Rietveld method using the General Structural Analysis System (GSAS). A transmission electron microscope (JEM-2100F, JEOL) at an operating voltage of 200 kV was used to obtain the high resolution transmission electron microscopy (HRTEM) images and elemental distributions. The room temperature excitation and emission spectra were measured by HITACHI F-7000 spectrometer. Diffuse reflection (DR) spectra were measured with a UV-vis-NIR spectrometer (UV 3600, Shimadzu). An FS5 fluorimeter (Edinburgh Instruments, Livingston, UK) was used to measure the fluorescence decays of Cr³⁺ and a 450 nm laser diode was used as an excitation source. The temperature dependent spectra were measured by the HITACHI F-7000 spectrometer and the temperature was controlled by a test device (TAP-02, Orient KOJI). The IQE and external QE (EQE) were recorded on Quantaurus-QY Plus C13534-12 quantum yield measurement system (Hamamatsu Photonics), where the IQE and EQE are defined as the ratio of the number of the photons emitted to the number of photons absorbed and excited, respectively. The photoelectric properties of the far-red pc-LEDs were measured using LHS-1000 (EVERFINE) equipped with high accuracy array spectrophotometer (350-1100 nm, HAAS-2000). The forward bias current for pc-LEDs was 10-150 mA. The photoelectric conversion efficiency is estimated by the ratio of the far-red light power of the emission (600-1100 nm) to the input electric power of LED.

3. Results and discussions

3.1. Structure analysis

XRD patterns of GAGG: $x \operatorname{Cr}^{3+} (x = 0.01, 0.04, 0.08)$ were identified and shown in Fig. 1a. All the diffraction peaks are well indexed to GAGG garnet structure that calculated by the Rietveld structural refinement



Fig. 2. (a) The room temperature excitation and emission spectra of GAGG: 0.04 Cr^{3+} ; (b) The emission spectra of GAGG: $x Cr^{3+}$ (x = 0-0.2) upon 450 nm excitation (c) and their emission intensities as a function of Cr^{3+} concentration; (d) Fluorescence decay curves of Cr^{3+} in GAGG: $x Cr^{3+}$ (x = 0.01-0.2) phosphors (excited at 450 nm, monitored at 720 nm).

(GSAS), as performed in Fig. 1a and b. Additionally, there is no extra peak appears in the patterns, indicating that pure phase GAGG: Cr^{3+} phosphors have been achieved. The diffraction peaks shift to lower angle with the increase of Cr^{3+} concentration, as shown in the magnified XRD patterns, because of the expansion of crystal lattice caused by substituting Al^{3+} ions (r = 0.54 Å, coordination number (CN) = 6) with larger Cr^{3+} ions (r = 0.62 Å, CN = 6). The Rietveld structural refinement of the XRD patterns of GAGG, GAGG: 0.01 Cr³⁺ and GAGG: 0.08 Cr³⁺ were performed to further examine the structure of GAGG: Cr³⁺ phosphors by using the crystallographic data of Gd₃Sc₂Ga₃O₁₂ (PDF# 82-1950) as a starting model [26]. To compare the changes in crystal structure because of the substitution of Al³⁺ with Cr³⁺, the XRD refinement of GAGG: *x* Cr^{3+} (*x* = 0.01, 0.08) with acceptable R factors (R_{wp}) as well as all of the XRD patterns were carried out in Fig. S1, and their crystallographic data and refinement parameters are summarized in Table S2. As displayed in Fig. 1c, GAGG: 0.08 Cr³⁺ belongs to a cubic space group of Ia3d (No. 230) with the lattice constants a = b = c =12.279 Å. Three types of sites exist in this garnet structure: Al³⁺ ions are dominantly coordinated with six O²⁻ to form [Al/GaO₆] octahedrons while Ga^{3+} ions are dominantly coordinated with four O^{2-} to form [Ga/AlO₄] tetrahedrons. Meanwhile, [Al/GaO₆] and [Ga/AlO₄] are connected with each other by sharing corners, which results in a three-dimensional network; Gd³⁺ is coordinated with eight O²⁻ to form [GdO₈] and locates in the dodecahedral site of the above network. It can also be concluded from the refinement results (see Table S3) that tiny amount Ga³⁺ ions occupy octahedral sites while Al³⁺ ions partly occupy tetrahedron sites. The result that larger Ga³⁺ prefers to occupy the smaller tetrahedron site is proved both experimentally and theoretically, and it is a consequence of not only the involvement caused by the interactions among Ga 3 d¹⁰ electrons but also a decrease of cation-cation repulsive force to stabilized the crystal structure due to the stronger covalency of Ga–O bond than Al–O bond [27–29]. In view of the same valence states as well as similar ionic radii between Cr^{3+} and Al^{3+} , we inferred that Cr^{3+} will prefer to substitute Al^{3+} ions in octahedral sites when Cr^{3+} ions are introduced into GAGG.

To confirm the lattice contraction, the fine structure observation of GAGG: 0.08 Cr^{3+} was performed by HRTEM. A good crystallinity of GAGG: 0.08 Cr^{3+} can be concluded from the distinct lattice fringes shown in HRTEM image in Fig. 1d. The distance between adjacent fringes is calculated to be 4.987 Å, which corresponds well with *d* (112) spacing (5.013 Å) of the refined structure of GAGG: 0.08 Cr^{3+} . Energy-dispersive X-ray spectroscopy (EDS) analysis (Fig. S2 and Table S4) was used to measure the chemical composition, and elemental distribution images of GAGG: 0.08 Cr^{3+} are also shown in Fig. 1e. Since the reaction temperature is high during the sintering process, an obvious agglomerate spheres can be found. The elemental distribution images indicate that Gd, Al, Ga, Cr, O are uniformly distributed in GAGG: 0.08 Cr^{3+} .

3.2. Photoluminescence properties

The room temperature emission and excitation spectra of GAGG: 0.04 Cr^{3+} were measured and depicted in Fig. 2a. Under 450 nm excitation, an emission band centered around 720 nm appears, which is attributed to the spin-allowed transition ${}^{4}\text{T}_{2} \rightarrow {}^{4}\text{A}_{2}$ of Cr^{3+} at a weak octahedral environment in GAGG. One may notice that the spectrum also consists the weak emission lines peaking at 697 nm and 716 nm, respectively, which are assigned to the ${}^{2}\text{E} \rightarrow {}^{4}\text{A}_{2}$ transitions of Cr^{3+} . The excitation spectrum monitored at 720 nm in GAGG: 0.04 Cr^{3+} is composed of two excitation bands at 450, and 625 nm, originating from the ${}^{4}\text{A}_{2} \rightarrow {}^{4}\text{T}_{1}$ (t²e), and ${}^{4}\text{A}_{2} \rightarrow {}^{4}\text{T}_{2}$ (t²e) transitions of Cr^{3+} , respectively [30–32], which is consistent with the found in the DR spectrum of GAGG: 0.04 Cr^{3+} (see Fig. S3). The crystal field strength parameter *Dq*



Fig. 3. (a) The integrated emission intensities of GAGG: $x \operatorname{Cr}^{3+}(x = 0.01, 0.04, 0.08)$ with the temperature elevated, and their corresponding emission spectra of (b) GAGG: 0.01 Cr^{3+} ; (c) GAGG: 0.04 Cr^{3+} and (d) GAGG: 0.08 Cr^{3+} under 450 nm excitation.

and Racah parameter *B* were calculated to show the crystal environment around Cr^{3+} ions and the relevant results are given in Supporting Information. The value of Dq/B is determined to be 2.76 in GAGG host, which is a slight larger than the so-called crossover point ($Dq/B \sim 2.3$), and resulting in Cr^{3+} locates at a medium crystal field strength site with the ²E state acting as the lowest excited state, thus, both the sharp line as well as relatively broadband emission are detected. The predominant excitation band peaking at 450 nm indicates that it could be efficiently excited by blue InGaN LED and its possible application as a far-red emitting phosphor for plant-growth lighting.

To further study the luminescence properties, a series of GAGG: $x \operatorname{Cr}^{3+}(x=0.01-0.2)$ were synthesized and their emission spectra as well as corresponding emission intensity are presented in Fig. 2b and c. The room temperature excitation spectra of GAGG: $x \operatorname{Cr}^{3+}(x=0-0.2)$ are also shown in Fig. S4. The emission intensity of Cr^{3+} is gradually enhanced with increasing x, and reaches the maximum at x = 0.08, and then (x > 0.08), the emission intensity decreases may due to concentration quenching caused by the well-known energy migration among Cr^{3+} ions at high concentration [33,34], which also leads to the slight red shift of the emission spectra. To give insight into the concentration quenching phenomena, the decay curves of Cr^{3+} in GAGG: $x \operatorname{Cr}^{3+}(x = 0.01-0.2)$ upon 450 nm excitation are depicted in Fig. 2d. The decay curve of Cr^{3+} gradually deviates from the single exponential profile with Cr^{3+} content, indicating the existence of the rarely involved ²E level with millisecond lifetime. The effective lifetime of Cr^{3+} is defined as:

$$T = \frac{\int_{0}^{\infty} tI(t)dt}{\int_{0}^{\infty} I(t)dt}$$
(1)

1

where I(t) is the intensity at time *t*. One can find from the inset in Fig. 2d, the effective lifetime monotonically decreases with Cr³⁺, which also

demonstrates the energy migration among Cr^{3+} ions.

The QE and corresponding measurement of GAGG: 0.08 Cr^{3+} were shown in Fig. S5, which is a key parameter to determine the possibility of the as-synthesized phosphors for LED application. The IQE and EQE of GAGG: 0.08 Cr^{3+} were measured to be as high as 94.1% and 38.6% while the absorption is 41.0% under 450 nm excitation. The higher IQE may be attributed to the good rigidity of garnet structure in GAGG [16, 35]. For detailed comparison, some luminescent properties concerning the reported Cr^{3+} doped phosphors are summarized in Table S1. The QE of GAGG: 0.08 Cr^{3+} is found to be the highest one among them, implying its great potential for pc-LEDs application.

3.3. Photoluminescence thermal stability

There is no doubt that temperature will greatly affect the luminescence properties, and the unavoidable emission loss caused by the heat generated during LED operation will limit the practical applications [36]. Therefore, appraising the thermal stability of GAGG: Cr^{3+} is necessary. The temperature dependences of the integrated emission intensities as well as their corresponding emission spectra in GAGG: $x \operatorname{Cr}^{3+}$ (x = 0.01, 0.04, 0.08) are shown in Fig. 3a–d. Although the emission peak intensity decreases continuously, as shown in Fig. 3a, the integrated emission intensity of Cr³⁺ gradually increases in temperature ranging from 30 °C to 90 °C (prominently from 30 °C to 210 °C for x =0.01), then declines slowly with further increasing the temperature and still maintains 76.3% even at 300 °C for x = 0.08, indicating a superior thermal stability of Cr³⁺ in GAGG. For phosphors with excellent thermal stability, their IQE usually remains unchanged below 150 $^\circ\text{C}.$ However, for \mbox{Cr}^{3+} (or $\mbox{Mn}^{4+}\mbox{)}$ whose absorption comes from the parity-forbidden d-d transitions, their absorption efficiency values are strongly dependent on the site symmetry; the larger the odd-parity crystal field is, the larger oscillator strength of the d-d transitions. It was also demonstrated that the oscillator strength of ${}^{4}A_{2} \rightarrow {}^{4}T_{2}$ transition can be enhanced with the increase of temperature due to the lowered site symmetry of Cr^{3+} by the thermally activated lattice vibration, which finally results in the



Fig. 4. (a) Photo of far-red pc-LED device fabricated by coating GAGG: 0.08 Cr^{3+} phosphor on a 460 nm blue LED; (b) Photos of lightened far-red pc-LED taken by a visible camera and (c) with a longpass filter at 550 nm; (d) Photo of lightened far-red pc-LED taken by a NIR camera with a longpass filter at 550 nm; (e) The electroluminescence spectrum of far-red pc-LED under a current of 100 mA. For comparison, the absorption spectra of P_{FR} and chlorophyll A are also given; (f) Far-red light power and photoelectric efficiency as a function of driving current of the fabricated far-red pc-LED. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

increased integrated emission intensity of Cr^{3+} and even higher than unity (just relative to that at room temperature) [37]. Such an anomalous thermal quenching behavior was also widely observed in other Cr^{3+} and Mn^{4+} (also d-d transitions) activated phosphors with high thermal stability [9,38,39]. Moreover, the full width at half maximum of the far red-emission band in GAGG: 0.08 Cr^{3+} (Fig. 3d) broadens from 68 to 107 nm as the temperature is elevated from 30 °C to 300 °C, which is attributed to the increasing temperature dependent electron-phonon interaction [38]. There is also a red shift of the emission band with increasing temperature, which may be due to the reduction of the crystal field strength because of the lattice expansion. To get more information about the thermal stability, the activation energy ΔE_a of GAGG: $x Cr^{3+}$ (x = 0.01, 0.04, 0.08) were calculated and given in Fig. S6. Obviously, large ΔE_a can be obtained with different Cr^{3+} concentration x, further indicating the excellent thermal stability of the as-synthesized samples.

3.4. Application to NIR pc-LEDs

A far-red pc-LED was fabricated by coating GAGG: 0.08 Cr^{3+} on a commercial 460 nm LED chip (0.5W) to display the performance of the phosphor, as shown in Fig. 4a. Photos of lightened far-red pc-LED taken by visible and NIR cameras are also shown in Fig. 4b-d, respectively. Fig. 4e shows the electroluminescence spectrum of the far-red pc-LED at a forward bias current of 100 mA (that of the prototype pc-LED under different currents is also shown in Fig. S7a). The emission spectrum consists of a strong far-red emission peaking at 720 nm and a narrow blue emission at 460 nm, matching well with the absorption bands of P_{FR} and chlorophyll A, respectively. The dependence of the far-red light power and photoelectric conversion efficiency of the fabricated far-red pc-LED device with driven currents are also shown in Fig. 4f. The farred light power is increased from 7.83 mW @ 10 mA to 61.03 mW @ 100 mA. In addition, the far-red photoelectric conversion efficiencies at 10 and 100 mA are calculated to be 30.1 (with an input power of 26.02 mW) and 20.6% (with an input power of 296.1 mW), which are higher than that of the reported far-red pc-LEDs (see Table S1). The above decrease in photoelectric conversion efficiency is mainly due to the "efficiency droop" of the blue LED chip (see Fig. S7b) [40]. The superior performance of the LED device indicates that GAGG: Cr³⁺ is an excellent candidate for the far-red LED toward plant-growth lighting.

4. Conclusions

In summary, far-red emission with high IQE (94.1%) was obtained in Cr^{3+} activated GAGG garnet phosphor. Moreover, the emission intensity of GAGG: Cr^{3+} can remain unchanged when the temperature is 150 °C, indicating it possesses an excellent thermal stability. Finally, the optimized GAGG: Cr^{3+} was employed to fabricated pc-LED with commercial 460 nm LED chip. The far-red light power is 61.03 mW under 100 mA driven current with a far-red photoelectric conversion efficiency as high as 20.6%, indicating its potential to serve as a far-red phosphor. Our results may indicate that GAGG: Cr^{3+} is a promising candidate for the far-red LED application in plant-growth lighting.

Prime novelty statement

In this paper, we developed an excellent far-red phosphor Gd_3Al_2 . Ga_3O_{12} : Cr^{3+} (GAGG: Cr^{3+}). Upon blue light excitation, GAGG: Cr^{3+} exhibits efficient far-red emission peaking at 720 nm with internal quantum efficiency as high as 94.1% and zero thermal quenching even at 150 °C. Moreover, a high-performance pc-LED device was fabricated by using the optimized GAGG: Cr^{3+} as the color converter, which can radiate 61.03 mW far-red light at 100 mA with a record photoelectric conversion efficiency of 20.6%. The results indicate that GAGG: Cr^{3+} holds great promise for plant-growth lighting and other LED applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlumin.2022.118750.

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