Near-Unity and Zero-Thermal-Quenching Far-Red-Emitting Composite Ceramics via Pressureless Glass Crystallization

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Laser-driven (LD) lighting is emerging as the next-generation high-power solid-state lighting technology. All-inorganic color converters with high quantum efficiency (QE), small thermal quenching, high thermal conductivity, and high thermal and chemical stabilities are crucial to coping with the enormous heat generated in LD lighting. Although luminescent translucent ceramics are the most promising class of color converters, only green/ yellow-emitting ones with satisfactory performance are developed before. Here, a far-red-emitting composite ceramics $Y_3AI_5O_{12}$ (YAG)-Al₂O₃:Cr³⁺ with near-unity internal QE and zero-thermal quenching are prepared via pressureless glass crystallization, where the inside light scattering is finely tuned by simply manipulating the temperature to induce controllable grain growth. The commonly used inert matrix Al₂O₃ here becomes an optically active component as YAG, thus alleviating the undesired concentration quenching while maintaining strong light absorption. Therefore, a high-power LD far-red lighting source with luminescence saturation threshold up to 21.4 W mm⁻² is demonstrated, which may find broad applications in plant growth lighting, solar simulators, and phototherapy.

1. Introduction

Phosphor-converted LEDs (pc-LEDs) have been widely used as the most efficient and cheapest solid-state lighting (SSL) sources

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in the fields of general white (visible) lighting and display backlighting.^[1] Driven by the booming demand for highend lighting sources in searchlight, automotive headlamp, and large-size projection displays-to name just a few, SSL devices are now advancing toward high power and special application.^[2] A significant limitation of pc-LEDs is the wellknown "efficiency droop" of LEDs that the efficiency of LEDs shows an obvious decrease at an input power density of only10 W cm⁻².^[3] To circumvent this, blue laser diodes that can retain their high efficiency at >30 kW cm⁻² have been proposed as an alternative excitation source. In such laser-driven (LD) lighting devices the irradiation of super-high blue photon flux causes the phosphors to generate a huge amount of heat, which, if not dissipated well, will result in strong thermal quenching of the phosphors and rapid degradation of the organic binders. Therefore, the

conventional phosphor–organic converters completely fail in this case owing to the low thermal conductivity ($\approx 0.2 \text{ W m}^{-1} \text{ K}^{-1}$) and the poor thermal and chemical stabilities of organic binders.^[2a,b] Developing all-inorganic color converters possessing high quantum efficiency (QE), small thermal quenching, high thermal conductivity, and high thermal and chemical stabilities simultaneously, becomes the key to boosting the applications of LD lighting.

Over the past 20 years several types of all-inorganic converters have been proposed, such as single crystals,^[4] single-phase or composite ceramics,^[5] and phosphor–glass composites.^[6] Although luminescent translucent ceramics are deemed to be the most promising one for LD lighting,^[2a,5a] they are limited to green and yellow light emission. Deep/far-red light (λ = 650 to 750 nm) not only is indispensable for full-spectrum white lighting,^[7] but also has broad applications in indoor or space agriculture,^[8] solar simulators,^[9] photobiomodulation therapy,^[10] and genome editing.^[11] Moreover, even if the internal QE (IQE) of a phosphor is 100%, the inevitable energy loss (i.e., the thermal relaxation of the phosphors) in the light conversion from blue to deep-red (far-red) is $\approx 30\%$ (40%), which is much higher than that ($\approx 20\%$) from blue to yellow. Unfortunately, all-inorganic deep/far-red-emitting converters with satisfactory properties have remained undiscovered so far, despite substantial progress in their powder-type counterparts.^[7,12]

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Figure 1. a) The transmission spectra of YAG–Al₂O₃ glass and ceramics (0.5 mm in thickness) annealed at different temperatures. The inset is the photographs of glass (the first on the left) and ceramics (the second to the last corresponding to 950 to 1350 °C). The SEM images of YAG–Al₂O₃ ceramics annealed at b) 950 °C, c) 1050 °C, d) 1150 °C, e) 1250 °C, and f) 1350 °C. g) The EBSD map of YAG–Al₂O₃ ceramic annealed at 1350 °C.

Ceramic materials such as Al₂O₃,^[5b,13] MgAl₂O₄,^[5c] CaF₂,^[5d] and hydroxyapatite^[5e] were recently explored as the matrix for Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺), the most widely used yellowemitting phosphor. In addition to their superior thermal and chemical stabilities, they can act as the favorable scattering center in LD lighting. In particular, Al₂O₃ possesses three times larger thermal conductivity (\approx 32 W m⁻¹ K⁻¹) than that of YAG $(\approx 10 \text{ W m}^{-1} \text{ K}^{-1})$,^[13] and one order of magnitude larger than that ($\approx 1.4 \text{ W m}^{-1} \text{ K}^{-1}$) of glasses^[6] and organic binders, which is extremely beneficial to the heat dissipation in LD lighting. Here, we report a far-red-emitting composite ceramic YAG-Al₂O₃:Cr³⁺ with near-unity IQE and zero-thermal quenching, prepared by using a pressureless glass crystallization method. We show that unlike those Ce³⁺ activated phosphor-glass/ceramic composites including YAG–Al₂O₃:Ce³⁺,^[5,6,13] Cr³⁺ ions can enter the octahedral Al³⁺ sites of Al₂O₃ as well as YAG so that Al₂O₃ matrix becomes an optically active component in YAG-Al₂O₃:Cr³⁺, besides playing the roles of heat sink, binder, and scattering center. Further, we demonstrate for the first time a high-power LD far-red lighting source by using YAG–Al₂O₃:Cr³⁺ as the color converter.

2. Results and Discussion

Translucent YAG–Al₂O₃ composite ceramics were usually prepared by using high pressure and high vacuum-assisted powder sintering techniques,^[5,13] which are tedious and expensive. A followed long-time (>10 h) annealing at 1450 °C in air is required to remove the oxygen vacancies formed in high vacuum and thus results in relatively low IQE and strong thermal quenching because of the partial oxidation of the activator ions like Ce³⁺ and Cr^{3+,[14]} Instead, we adopted a pressureless glass crystallization technique that has been used to achieve fully dense nanocrystalline ceramics with high transparency^[13d,15] to prepare translucent YAG–Al₂O₃:Cr³⁺ ceramics. Considering the glass-forming ability,^[13d,16] the compositions of the raw materials for the glass precursors were set to 26 mol%Y₂O₃-(74-*x*) mol%Al₂O₃-*x* mol%Cr₂O₃ (YAG–Al₂O₃:*x*%Cr³⁺), which means the polycrystalline ceramics fully crystallized from the glasses consist of 77 wt% YAG and 23 wt% Al_2O_3 , assuming the substitution of Al^{3+} by Cr^{3+} . Transparent bulk glasses were synthesized using an aerodynamic levitation system equipped with two CO_2 lasers (Figure S1, Supporting Information). Such a containerless method enables high-temperature melting (≈ 2000 °C) and rapid cooling (≈ 300 °C s⁻¹) to prepare YAG– Al_2O_3 :x%Cr³⁺ glasses without contamination (Figures S1 and S2, Supporting Information).^[15–17]

When the parent glasses are annealed at >950 °C for 2 h, they fully crystallize into YAG-Al₂O₃ ceramics (Figure S2, Supporting Information). The total transmittance (81.7% at 450 nm) of YAG-Al₂O₃ ceramic annealed at 950 °C is comparable to the parent glass (85.3% at 450 nm) (Figure 1a), indicating that the grain growth is suppressed near the crystallization temperature (Figure S3, Supporting Information) and the light scattering is thus minimized by the nanosized YAG and Al₂O₃ crystalline grains (Figure 1b-f).^[13d,15] Higher annealing temperatures lead to transparency reduction of YAG-Al₂O₃ ceramic, especially in the shortwavelength range, and the crystalline grains grow from dozens of nanometers to sub-micrometer as the annealing temperature is elevated to 1350 °C. Meanwhile, Al₂O₃ undergoes a successive phase transformations, changing from δ -phase to θ -phase at \approx 1150 °C and from θ phase to α -phase at >1250 °C (Figure S2, Supporting Information), which was discussed in detail by Ma et al.^[13d] Considering that very limited pores exist in the translucent YAG-Al₂O₃ (Figure 1b-f), the transparency reduction is mainly attributed to the enhanced Rayleigh scattering owing to the grain growth activated by higher temperatures.^[15] Besides, the electron backscattered diffraction (EBSD) (Figure 1g) and the energy dispersive spectroscopy (EDS) mapping (Figure S4, Supporting Information) clearly reveal that nanosized Al₂O₃ is uniformly distributed at the grain boundary of sub-micrometer-sized YAG particles in the translucent YAG–Al₂O₃.

The ultrahigh light power density of the focused incident laser in LD lighting necessitates strong light scattering to improve the light extraction and the color uniformity, which is quite opposite to pc-LEDs.^[2a,13,18] The management of light scattering is, however, impossible for single crystals, and also difficult www.advancedsciencenews.com

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Figure 2. a) The emission spectra of YAG–Al₂O₃:0.6%Cr³⁺ ceramics annealed at different temperatures. The inset is their photographs under white light (left) and 420 nm light (right). b) Schematic diagram of concentration quenching. Left is that activators like Ce³⁺ can only be doped into YAG. Right is that Cr³⁺ can be homogeneously distributed in YAG and Al₂O₃. Small interionic distance in the former allows the transfer of excitation energy to the luminescence killers, i.e., concentration quenching. c) IQE of YAG–Al₂O₃:0.6%Cr³⁺ ceramics annealed at different temperatures. d) The decay curves and the calculated average lifetimes of YAG–Al₂O₃:0.6%Cr³⁺ ceramics annealed at different temperatures.

for ceramics when using the traditional powder sintering. As shown above, the mismatched refractive index between Al_2O_3 (1.76) and YAG (1.82)^[13d] make it very easy to regulate the light scattering inside YAG– Al_2O_3 ceramic by simply controlling the temperature field to induce the desired grain growth. It is worth mentioning that ceramic green body for the powder sintering is highly porous while the parent glass is fully dense for glass crystallization used here, suggesting that the latter may be a more feasible strategy for preparing ceramic color converters and managing the light scattering therein.

YAG–Al₂O₃:Cr³⁺ shows typical far-red emission of Cr³⁺ (**Figure 2a**) under deep-blue light excitation, and the optimum doping concentration was determined to be 0.6 mol%. One of the broad absorption/excitation bands originating from the spin-allowed ⁴A₂→⁴T₁ transition of Cr³⁺ locates in the spectral range of 380–500 nm, which matches well with the emission of the efficient blue LEDs and laser diodes (Figures S5 and S6, Supporting Information). Generally, Cr³⁺ exclusively enters the octahedrally coordinated sites due to its large crystal field stabilization energy, and both of YAG and Al₂O₃ crystals have only one kind of octahedral Al³⁺ site available for Cr³⁺.⁽¹⁹⁾ The emission spectrum of Cr³⁺ in AlO₆ octahedron with strong crystal field typically

consists of a dominant R-line emission (zero-phonon ${}^{2}E \rightarrow {}^{4}A_{2}$ transitions) and several sidebands associated to phonon-assisted transitions, and the position of R line is strongly dependent on the crystal field.^[19] These enable us to identify the origin of Cr³⁺ emission and thus the phase transition in YAG-Al₂O₃ annealed at different temperatures. As shown in Figure 2a and Figure S7 (Supporting Information), the characteristic R line (689 nm) of YAG:Cr³⁺ nearly dominates all the emission spectra no matter what annealing temperature is, which is expected as YAG is the main phase (77 wt%) in YAG-Al₂O₃ ceramics (Figure S2, Supporting Information). There is a trade-off between the R lines of θ -Al₂O₃:Cr³⁺ (684 nm)^[19] and α -Al₂O₃:Cr³⁺ (695 nm) when the annealing temperature is higher than 1250 °C, confirming the occurrence of phase transition from θ - to α -Al₂O₃. Notably, no peaks belonging to θ -Al₂O₃ can be found in the XRD patterns (Figure S2, Supporting Information) of YAG-Al₂O₃:Cr³⁺ annealed at 1350 °C for 2 h by us as well as Ma et al.,^[13d] whereas the intensity of R line at 684 nm indicative of θ -Al₂O₃:Cr³⁺ is still very high (Figure 2a) and prolonging the annealing time can obviously lower its intensity (Figure S8, Supporting Information), indicating that the phase transformation of θ -Al₂O₃ is markedly retarded in YAG-Al₂O₃. The absence of diffraction

peak of θ -Al₂O₃ in XRD pattern may be due to the faster grain growth of YAG and α -Al₂O₃ than that of θ -Al₂O₃.

Compared with single crystals and single-phase translucent ceramics, phosphor-glass/ceramic composites allow diverse selection of phosphors and matrix compositions,^[5,6] where the matrix materials can play the roles of binder, scattering center, and heat sink. In the previously reported composites, the matrix such as Al₂O₃,^[13] CaF₂,^[5d] and silicate glasses,^[6] is nonluminescent (inert) or will become luminescence killers if the undesired interfacial reaction occurs. For strong light absorption, the concentration of the associated activators inside the active component should thus be as high as in phosphor powders, which inevitably leads to unsatisfactory IQE and stronger thermal quenching owning to the (thermally activated) concentration quenching,^[20] as schematically illustrated in Figure 2b. By contrast, Cr³⁺ can be uniformly distributed and efficiently emitting in Al₂O₃ and YAG. Thus, the detrimental effect of concentration quenching can be largely relieved in YAG-Al₂O₃:Cr³⁺, which is supported by its near-unity IQE and zero-thermal quenching.

With the annealing temperature increasing from 950 to 1350 °C, the IQE of YAG-Al₂O₃:0.6%Cr³⁺ ceramic can be significantly improved from 10.5% to nearly 100% (Figure 2c), which is a record value for the deep/far-red-emitting color converters including phosphors (see Table S1 of the Supporting Information for a detailed comparison). The average lifetime (Figure 2d) of the excited level ${}^{2}E$ of Cr^{3+} is correspondingly prolonged from 0.53 to 2.04 ms, suggesting that nonradiative transitions were suppressed in YAG-Al₂O₃:Cr³⁺ annealed at higher temperatures. In addition to the improved crystalline property and the reduced surface defects because of larger grain size, the reduction of Cr⁴⁺ to Cr³⁺ (Figure S5, Supporting Information) at higher temperatures is responsible for the improvement of IQE.^[2d] Moreover, YAG-Al₂O₃:Cr³⁺ ceramics have a higher absorption of blue light, as compared with traditional YAG: Cr^{3+} and α -Al₂O₃: Cr^{3+} powders with the same doping concentration (Table S2, Supporting Information). This is due to the weaker light scattering in fully dense ceramics with reasonable light transmittance (Figure 1a). The EQE of YAG-Al₂O₃:0.6%Cr³⁺ can reach as high as 58.3%, which is much higher than that (<40%) of Cr^{3+} activated phosphors.^[2d,2e]

One of the major problems faced by phosphor-converted SSL devices is that the unavoidable heat in the light conversion will push up the operating temperature to 150 °C or much higher in high-power operation.^[2a] IQE loss of phosphors at high temperatures, i.e., thermal quenching, can further increase the temperature, resulting in serious performance deterioration. To overcome such a thermal runaway effect, it demands phosphors with thermal quenching as small as possible, in addition to external heat sinks with high thermal conductivity. From the temperature-dependent emission spectra of YAG-Al₂O₂:Cr³⁺ (Figure 3a; Figure S9, Supporting Information), we can see that the samples annealed at lower temperature suffer from stronger thermal quenching, and an annealing temperature of 1350 °C endows YAG-Al₂O₃:Cr³⁺ with zero-thermal quenching even at 300 °C, which is essentially consistent with the results of IQE. In spite of no decrease of the emission intensity, the decay rate of YAG-Al2O3:Cr3+ annealed at 1350 °C becomes faster with increasing the temperature (Figure S10, Supporting Information). This counterintuitive behavior of Cr³⁺ emission



Figure 3. a) The integrated emission intensities of YAG-Al₂O₃:0.6%Cr³⁺ ceramics annealed at different temperatures as a function of the temperature. b) Schematic diagram of excited states of Cr³⁺ at higher temperatures. The excited electrons in ²E level can be thermally populated into a higher ⁴T₂ level, thus leading to faster depopulation due to the spinallowed ⁴T₂→⁴A₂ transitions.

also exists in YAG:Cr³⁺ and Al₂O₃:Cr³⁺ powders (Figure S11, Supporting Information), and can be well explained by the simplified Tanabe-Sugano diagram in Figure 3b. The relative energy positions of ⁴T₂ and ²E states of Cr³⁺ vary with the crystal field strength of the host crystals. In YAG and Al₂O₃ with strong crystal field, the ⁴T₂ state is higher than the ²E state, and ⁴T₂→⁴A₂ transition will be more possible at higher temperatures because of the thermal population of ⁴T₂ state. Considering the negligible nonradiative transitions in the temperature range of interest, the faster decay of Cr³⁺ at higher temperature is mainly attributed to the two orders of magnitude larger radiative rate of the spin-allowed ⁴T₂→⁴A₂ than the spin-forbidden ²E→⁴A₂ transitions.^[19] In addition, large radiative rate of Cr³⁺ can also theoretically improve its resistance against thermal quenching to some extent given the same local structure. SCIENCE NEWS ______ www.advancedsciencenews.com





Figure 4. a) Photos of the as-fabricated far-red-emitting pc-LED device (left) and the lighted one in the darkness (right). b) The electroluminescent spectrum of the as-fabricated far-red-emitting pc-LED. The absorption spectra of chlorophyll-a and P_{FR} are also shown for comparison. c) Far-red light power and far-red photoelectric efficiency as a function of the operating current. d) Luminescence spectra of YAG–Al₂O₃:0.6%Cr³⁺ (5 mm in diameter, 1.0 mm in thickness) under different laser operating currents. e) Far-red light output power of YAG–Al₂O₃:x%Cr³⁺ ceramics (1 mm in thickness) annealed at 1350 °C with different Cr³⁺ concentrations as a function of the incident blue laser power density in a reflective mode. Note that the detected data for YAG–Al₂O₃:0.2%Cr³⁺ is because the unabsorbed blue laser light is beyond the saturation of the detector, which does not exist in the transmissive mode (Figure S14, Supporting Information). f) Photo of the as-fabricated LD far-red flashlight. Right is the photo of the lighted characters 5 m away from the flashlight.

To evaluate the conversion capability of YAG-Al₂O₃:Cr³⁺ in practical SSL applications, we fabricated a far-red-emitting pc-LED (Figure 4a) by combing 1 W 420 nm LED chips with YAG-Al2O3:0.6%Cr3+ annealed at 1350 °C. The as-fabricated pc-LED exhibits dual emissions at 420 and 708 nm (Figure 4b), which overlap well with the absorption bands of chlorophyll-a and the active state of phytochrome (P_{FR}), respectively; chlorophyll-a participates in harvesting light to drive photosynthesis while P_{FR} is critical to photomorphogenesis;^[8] therefore, it has great potential for plant growth lighting. The photoelectric efficiency, the ratio of the far-red light power to the input electric power, is as high as 21% at a driving current of 20 mA (Figure 4c), approaching the theoretical limit ($\approx 25\%$) of this kind of pc-LED devices. The monotonous decrease of photoelectric efficiency with the current is due to the "efficiency droop" of LED chip (Figure S12, Supporting Information).^[21]

Together with the high thermal conductivity ($\approx 10 \text{ W m}^{-1} \text{ K}^{-1}$) of YAG–Al₂O₃,^[13c] near-unity IQE and zero-thermal quenching make YAG–Al₂O₃:Cr³⁺ an excellent color converter for LD lighting. We adopted a reflective mode to further demonstrate its performance in LD lighting (Figure S13, Supporting Information).

As shown in Figure 4d,e, the converted far-red light power increases first with the blue laser excitation power, and then reaches a maximum for YAG-Al₂O₃:0.6%Cr³⁺ at the excitation power (density) of 10.7 W (21.4 W mm⁻²), implying the occurrence of the luminescence saturation at this point. The luminescence saturation occurs earlier for YAG-Al₂O₃:1.0%Cr³⁺ (15.7 W mm⁻²) and no saturation is observed for YAG-Al₂O₃:0.2%Cr³⁺ within the peak power of the used blue laser (also see the data in a transmissive mode in Figure S14, Supporting Information), which is ascribed to the stronger thermal quenching (Figure S15, Supporting Information) as well as the higher light absorption (Table S2, Supporting Information) of the former. The saturation threshold of YAG-Al₂O₃:0.6%Cr³⁺ is one order of magnitude larger than other red-emitting composites^[22] and also comparable to those yellow-emitting ceramics.^[5,13] Note that the laser irradiation point of phosphor-organic composite will be carbonized even at 1 W mm⁻¹ because the temperature is raised to more than 400 °C by the accumulated heat (Figure S16, Supporting Information). Finally, as displayed in Figure 4f, a prototype of LD far-red flashlight fabricated by combining YAG-Al₂O₃:0.6%Cr³⁺ with a 450 nm laser diode (5 W) can illuminate the characters

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5 m or more away (Figure S17 and Video S1, Supporting Information), which may find broad applications in lighting fields.^[23]

3. Conclusion

In summary, we have developed a far-red-emitting translucent composite ceramic YAG–Al₂O₃:Cr³⁺ via the pressureless glass crystallization. The concentration quenching in composite color converters is alleviated by optically active matrix Al₂O₃:Cr³⁺. Near-unity IQE, zero-thermal quenching and strong light absorption have been simultaneously achieved in YAG– Al₂O₃:Cr³⁺, whereby a high-performance LD far-red lighting source has been demonstrated for the first time. It is also demonstrated that pressureless glass crystallization enables the simple and economical preparation of fully dense ceramics with highly controllable light scattering, which will inaugurate a new strategy for developing ceramic-based color converters for compact pc-LEDs and LD lighting.

4. Experimental Section

See the Supporting Information for experimental details.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

W.X. conceived the idea and designed the experiments. J.Q. supervised the project. G.Z., H.W., and J.W. performed the experiments and collected the data. W.X., G.Z., J.Q., and X.L. analyzed the data and discussed the results. W.X. and G.Z. wrote the manuscript with input from others.

Data Availability Statement

Research data are not shared.

Keywords

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