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Xu, Jian; Tanabe, Setsuhisa; Sontakke, Atul D.; Ueda, Jumpei


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Jian Xu, Setsuhisa Tanabe, Atul D. Sontakke, and Jumpei Ueda
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

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We developed a persistent phosphor of Y\(_3\)Al\(_2\)Ga\(_3\)O\(_{12}\) doped with Nd\(^{3+}\), Ce\(^{3+}\), Cr\(^{3+}\) ions (YAGG:Nd-Ce-Cr) exhibiting long (>10h) persistent luminescence at multi-wavelengths of around 880, 1064, and 1335 nm due to f-f transitions of Nd\(^{3+}\) and at 505 nm due to Ce\(^{3+}:5d_{1}→4f\) transition. The intense near-infrared (NIR) persistent luminescence bands from Nd\(^{3+}\) match well with the first (650–950 nm) and second (1000–1400 nm) bio-imaging windows. The NIR persistent radiance of the YAGG:Nd-Ce-Cr phosphor (0.33 × 10\(^{-1}\) mW/Sr/m\(^2\)) at 60 min after ceasing blue light illumination was over 2 times higher than that of the widely used ZnGa\(_2\)O\(_4\):Cr\(^{3+}\) red persistent phosphor (0.15 × 10\(^{-1}\) mW/Sr/m\(^2\)).

Recently, persistent phosphors (sometimes named as long-lasting phosphors) have attracted much attention for in vivo bio-imaging applications since these nano-particle phosphors charged by ultraviolet (UV) light (visible light in rare cases) before injection into biological tissues can emit red and/or near-infrared (NIR) persistent luminescence lasting for minutes to even several hours without further real-time illumination.\(^{1–4}\) The exclusion of external illumination for minutes to even several hours without further real-time illumination (only few of them are suitable for the NIR-II window) and long-term phosphors can be promising candidates for bio-imaging, materials emitting in the NIR region, especially in the NIR-II window.\(^{1000–1400 \text{ nm}}\) has promising advantages owing to its lower autofluorescence, deeper tissue penetration, and thus potentially higher spatial and temporal resolution than the NIR-I window.\(^{5–8}\) Till now, although several types of optical probes for the NIR-II window have been developed such as single-walled carbon nanotubes,\(^{16}\) and semiconductor quantum dots composed of highly toxic heavy metals,\(^{17}\) the development of nontoxic and biocompatible luminescent materials emitting in the NIR region, especially in the NIR-II window, still remains a challenge. Although persistent phosphors can be promising candidates for bio-imaging, only few of them are suitable for the NIR-II window and their persistent durations are quite short (only up to few minutes),\(^{18–20}\) which limits their practical applications.

Recently, a garnet persistent phosphor of Ce\(^{3+}\), Cr\(^{3+}\) co-doped Y\(_3\)Al\(_2\)Ga\(_3\)O\(_{12}\) (YAGG:Ce-Cr) has been developed by our group.\(^{21–24}\) In this material, Cr\(^{3+}\) acts as an electron trap with ideal trap depth at x = 3 for persistent luminescence of Ce\(^{3+}\) working at room temperature (RT). Based on our previous work, we developed a persistent phosphor of Y\(_3\)Al\(_2\)Ga\(_3\)O\(_{12}\):Nd\(^{3+}\), Ce\(^{3+}\), Cr\(^{3+}\) (YAGG:Nd-Ce-Cr). This material can be excited by blue light (460 nm) and emit green persistent luminescence due to Ce\(^{3+}:5d_{1}→4f\) for over 10h. Furthermore, thanks to the highly efficient energy transfer (ET) from Ce\(^{3+}\) to Nd\(^{3+}\) in garnet hosts,\(^{25–27}\) it can also show NIR persistent luminescence for almost the same duration due to Nd\(^{3+}:F_{2}→^{4}I_{9/2}, {^{4}I}_{11/2}, {^{4}I}_{13/2}\) transitions, matching well with the NIR-I and NIR-II windows. A persistent phosphor with such a wide emission range (green to NIR) and long (>10h) persistent duration has never been reported before and we thus state as a discovery.

YAGG:Nd-Ce-Cr and YAGG:Nd cerium phosphors with the composition of Y\(_2.985\)Ce\(_{0.015}\)Al\(_{1.999}\)Cr\(_{0.001}\)Ga\(_3\)O\(_{12}\) and Y\(_2.97\)Nd\(_{0.03}\)Al\(_2\)Ga\(_3\)O\(_{12}\), respectively, were fabricated by a solid-state reaction method. Y\(_2O_3\) (99.99%), Al\(_2O_3\) (99.99%), Ga\(_2O_3\) (99.99%), Ce\(_2O_3\) (99.99%), Nd\(_2O_3\) (99.99%), and Cr\(_2O_3\) (99.9%) were used as raw materials. The starting powder was mixed by ball milling method with anhydrous alcohol for several hours. The mixed powder was dried at 80°C for 36 h, compacted to form a ceramic green body (ϕ20 mm, 2 mm thickness) under uniaxial pressing of 50 MPa, and finally sintered at 1600°C for 24 h in air. The YAGG:Ce-Cr (Y\(_2.985\)Ce\(_{0.015}\)Al\(_{1.999}\)Cr\(_{0.001}\)Ga\(_3\)O\(_{12}\)) ceramic phosphor prepared by the same experimental procedure was used as a reference sample.\(^{22}\)

The diffuse reflectance spectra of the ceramic samples were measured by a spectrophotometer (UV3600, Shimadzu) equipped with an integrating sphere. Photoluminescence (PL) spectra of the YAGG:Ce-Cr and YAGG:Nd-Ce-Cr samples were recorded in the range of 400–1600 nm by pumping with a 442 nm laser diode (NDH510APA-E, Nichia Co. Ltd.), excitation. The PL spectra were measured by a monochromator (G250, Nikon), a Si photodiode (PD) detector (S-025-H, Electro-Optical System Inc.) from 400 to 800 nm and an InGaAs PD detector (IGA-030-H, Electro-Optical
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Comparing the PL spectrum of the YAGG:Ce-Cr sample with the decay curves were calibrated to the absolute luminance PD. In order to monitor the Ce$^{3+}$ value–1600, and aperture value (F value)–5.0.

PersL spectra of the YAGG:Ce-Cr and YAGG:Nd-Ce-Cr samples under blue laser (442 nm) excitation are shown in Fig.1(b). The persistent emission bands exhibit all but the Nd$^{3+}$ luminescence. Then the decay curves were calibrated to the absolute luminance (in unit of mcd/m$^2$) using a radiance meter (Glacier X, B&W Tek Inc.). In order to monitor the Nd$^{3+}$ luminescence, the Si PD was covered with an 800 nm short-cut filter to filter out all but the Nd$^{3+}$ luminescence. Then the decay curves were calibrated to the absolute radiance (in unit of mW/Sr/m$^2$) using the same radiance meter. Photographs of the samples were taken by a digital camera (EOS kiss X5, Canon), and the settings remained constant: exposure time–5 s, ISO value–1600, and aperture value (F value)–5.0.

Fig. 1(a) shows the PL spectra of the YAGG:Ce-Cr and YAGG:Nd-Ce-Cr samples under blue laser (442 nm) excitation. The YAGG:Ce-Cr sample exhibits an intense emission band centered at 505 nm, corresponding to the f-d transition of the lowest 5d energy level (5d$_{1}$) to the 4f ground state of Ce$^{3+}$. Besides, a weak emission band at around 690 nm is assigned to the $^2$E $\rightarrow$ $^4$A$_2$ transition (R-line) of Cr$^{3+}$.

The PersL spectra of the YAGG:Ce-Cr sample with the diffuse reflectance of the Nd$^{3+}$ singly doped YAGG sample (YAGG:Nd), the absorption bands ($^4$I$_{9/2} \rightarrow ^2$G$_{3/2}$, $^4$G$_{7/2}$, $^2$G$_{5/2}$) of Nd$^{3+}$ are overlapped with the emission range of Ce$^{3+}$ indicating that the ET process from Ce$^{3+}$ to Nd$^{3+}$ can efficiently occur. This is confirmed by the decrease of Ce$^{3+}$ emission intensity in the visible range and the presence of several sharp emission bands at around 880 nm, 1064 nm, and 1335 nm owing to the f-f transitions of Nd$^{3+}$: $^4$F$_{3/2}$ $\rightarrow$ $^4$I$_{9/2}$, $^4$I$_{11/2}$, and $^4$I$_{13/2}$, respectively, in the YAGG:Nd-Ce-Cr sample.

The PersL spectra of the YAGG:Nd-Ce-Cr sample recorded at different times after ceasing blue illumination are shown in Fig. 1(b). The persistent emission bands exhibit not only a broad band located at around 500 nm due to Ce$^{3+}$: 5d$_1$ $\rightarrow$ 4f transition but also intense sharp bands located at the NIR region (around 880 nm, 1064 nm, and 1335 nm) due to the f-f transitions of Nd$^{3+}$, which match well with the NIR-I and NIR-II windows. The identical shape of its PL and PersL spectra suggests that the emission centers are the same under and after excitation. Since the ET process from Ce$^{3+}$ to Nd$^{3+}$ occurs in PL, we assume that the similar energy transfer process called persistent energy transfer (persistent ET) also occurs in the YAGG:Nd-Ce-Cr phosphor after ceasing the excitation source. The phenomenon of the persistent ET has been confirmed previously in CaAl$_2$O$_4$:Tb$^{3+}$:Ce$^{3+}$ (Refs. 28 and 29) and Sr$_4$Al$_{14}$O$_{25}$:Cr$^{3+}$, Eu$^{2+}$, Dy$^{3+}$ (Ref. 30) persistent phosphors.

The persistent luminescent decay curve monitoring Ce$^{3+}$ emission (475–650 nm) of the YAGG:Nd-Ce-Cr sample after ceasing blue light illumination is shown in Fig. 2(a), in which the decay curves of the standard YAGG:Ce-Cr ceramic phosphor and a compacted ceramic pellet made of the well-known SrAl$_2$O$_4$:Eu$^{2+}$-$\text{Dy}^{3+}$ (SAO:Eu-Dy) commercial phosphor (LumiNova- GLL300FFS, Nemoto & Co. Ltd.) under the same experimental condition are also plotted as references.22 The luminance values at 60 min after ceasing the excitation are 11 mcd/m$^2$ for YAGG: Nd-Ce-Cr, 30 mcd/m$^2$ for YAGG:Ce-Cr, and 25 mcd/m$^2$ for SAO:Eu-Dy, respectively (see the photographs of the two ceramics under and after blue LED illumination in Fig. 2(d)). Persistent luminescence durations to reach a luminance of 0.32 mcd/m$^2$ in the YAGG:Nd-Ce-Cr ceramic is around 688 min, which is comparable with but slightly shorter than that of the
YAGG:Ce-Cr (about 808 min) ceramic, due to quenching of visible Ce$^{3+}$ emission by the ET to Nd$^{3+}$. Note that the luminance value 0.32 mcd/m$^2$ is the minimum value commonly used by the safety signage industry (about 100 times the sensitivity of the dark-adapted eye). Because of this long green persistent luminescence at wavelengths very sensitive to the human’s photopic vision, the YAGG:Nd-Ce-Cr nano-sized phosphor synthesized by nano-technical methods can act as a fluorescence marker convenient for surgeons to roughly confirm or even trace the marked tissues directly by human eyes without any electronic detectors in the difficult conditions typical of surgery dissection.

The persistent luminescent decay curve monitoring Nd$^{3+}$ emission (>800 nm) of the YAGG:Nd-Ce-Cr sample after ceasing the same illumination is shown in Fig. 2(b), in which the decay curve of the standard ZnGa$_2$O$_4$:Cr$^{3+}$ (ZGO:Cr) ceramic under the same experimental condition is also plotted as a reference. The NIR radiance value of the tri-doped sample at 60 min after ceasing the blue excitation (0.33 × 10$^{-1}$ mW/Sr/m$^2$) is over 2 times higher than that of the widely used red persistent phosphor, ZGO:Cr (0.15 × 10$^{-1}$ mW/Sr/m$^2$), indicating that this phosphor exhibits superior persistent luminescence both in the visible (Ce$^{3+}$ emission) and NIR (Nd$^{3+}$ emission) ranges.

The decay profiles of the Ce$^{3+}$ and Nd$^{3+}$ are quite similar in Figs. 2(a) and 2(b). The persistent radiance ratio (Nd$^{3+}$/Ce$^{3+}$) is plotted against the monitoring time of the whole decay curve as shown in Fig. 2(c). The result clearly suggests that the ratio remains almost constant (around 112%–114%) with time, which supports that the persistent luminescence from both ions originates from common electron trapping and de-trapping processes, where the NIR persistent luminescence of Nd$^{3+}$ is due to the persistent ET process from Ce$^{3+}$ to Nd$^{3+}$ in the garnet host.

Fig. 3 shows the two-dimensional (2D) mappings of TL glow curves of the YAGG:Ce-Cr and YAGG:Nd-Ce-Cr samples in order to see what kind of emission contributes to the TL glow peak at different temperatures. From the contour plot of the YAGG:Ce-Cr sample in Fig. 3(a), it can be seen that at increased temperatures, the TL spectrum is simply composed of two emission bands from Ce$^{3+}$ and Cr$^{3+}$. While in the YAGG:Nd-Ce-Cr sample (see Fig. 3(b)), the NIR emission of Nd$^{3+}$ appears at the same time due to the persistent ET process, which agrees well with its PersL.
The persistent luminescence mechanism of the YAGG:Nd-Ce-Cr phosphor is briefly explained by constructing the vacuum referred binding energy (VRBE) diagram, composed of Ce\(^{3+}\), Nd\(^{3+}\), Cr\(^{3+}\), CB, and valence band energy levels in the Y\(_3\)Al\(_2\)Ga\(_3\)O\(_{12}\) host (see Fig. 4). When the YAGG:Nd-Ce-Cr sample is charged by blue light, Ce\(^{3+}\) is promoted from the ground state to the 4F\(_{5/2}\) excited level, and then finally induces the sharp luminescence bands of Nd\(^{3+}\). Since its NIR persistent luminescence bands match well with the NIR-I and NIR-II bio-imaging windows, multi-functional applications not only in the in vivo bio-imaging but also in the drug delivery and cancerous chemotherapy can be expected in the near future by using this material as a nano-sized bio-probe with surface modification connected with functional organic radical groups.

We would like to acknowledge Professor Bruno. Viana who stayed at Kyoto University as a visiting professor for fruitful discussion on persistent phosphors and bio-imaging.

![Diagram of VRBE for Ce\(^{3+}\), Nd\(^{3+}\), and Cr\(^{3+}\) energy levels in Y\(_3\)Al\(_2\)Ga\(_3\)O\(_{12}\) (YAGG) host.](image)

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