Near infrared long-persistent phosphorescence in La$_3$Ga$_5$GeO$_{14}$:Cr$^{3+}$ phosphor

Wuzhao Yan,$^{1,2}$ Feng Liu,$^{1}$ Yi-Ying Lu,$^{1}$ Xiao-Jun Wang,$^{3}$ Min Yin,$^{2}$ and Zhengwei Pan$^{1,4}$

$^{1}$Department of Physics, University of Georgia, Athens, Georgia 30602, USA
$^{2}$Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China
$^{3}$Department of Physics, Georgia Southern University, Statesboro, Georgia 30460, USA

*panz@uga.edu

Abstract: Near infrared (NIR; 660–1300 nm) long-persistent phosphorescence from Cr$^{3+}$ ions with persistence time of more than 1 hour was realized in La$_3$Ga$_5$GeO$_{14}$:Cr$^{3+}$ phosphor (with or without co-dopants such as Li$^+$, Zn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$ and Dy$^{3+}$). The NIR phosphorescence can be effectively achieved under UV illumination (~240–360 nm) but is barely achieved by blue light (~480 nm) irradiation, even though the blue light excitation are effective to the NIR fluorescence. The NIR phosphorescence mechanisms were discussed by measuring the irradiation energy dependence of the phosphorescence intensity.

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References and links

1. Introduction

Long-persistent phosphorescence phenomena have been known for decades, and the investigation of long-persistent phosphors is becoming one of the most attractive subjects in the phosphor field [1]. Long-persistent phosphors in visible region have been well developed and have been widely applied in various important fields as security signs, emergency route signs, safety indication, and indicators of control panels in dark environments or in the night [2]. The research and development of long-persistent phosphors in the near infrared (NIR) region, in contrast, are far behind their visible counterparts, even though there are increasing demands in recent years for applications as identification markers in defense and security and as optical probes in in vivo bio-imaging [2,3]. Up to now, only a few studies related to NIR long-persistent phosphors were reported [3,4], which were mainly co-doped (e.g., Eu$^{2+}$ and Eu$^{3+}$–Er$^{3+}$) phosphors designed basing on persistent energy transfer mechanism. However, the limited energy transfer efficiency and the inevitable visible phosphorescence from the donor ions (e.g., green emission from Eu$^{3+}$) hinder the further investigations of these phosphors.

In design of NIR phosphors, trivalent chromium ion (Cr$^{3+}$) is a favorable choice of activation center because the luminescence wavelengths of Cr$^{3+}$-activated phosphors, from 660 to 1300 nm depending on the crystal field strength of the host lattices, meets the requirement of many technological applications. In the development of Cr$^{3+}$-activated NIR tunable laser crystals, gallates were usually used as the host materials since the Cr$^{3+}$-doped gallates show strong NIR emission. The reported Cr$^{3+}$-doped gallates include Ln$_2$Ga$_5$O$_{12}$:Cr$^{3+}$ (Ln = Y, Gd, La or Lu) [5], LiGa$_5$O$_6$:Cr$^{3+}$ [6], Mg$_5$Ga$_3$Ge$_2$O$_{14}$:Cr$^{3+}$ (M = Sr or Ca) [7], La$_3$Ga$_5$Si$_2$O$_{12}$:Cr$^{3+}$ [8], La$_2$Ga$_4$Zn$_{1}$O$_{12}$:Cr$^{3+}$ [9], and La$_2$Ga$_5$Ge$_2$O$_{14}$:Cr$^{3+}$ [10]. Even though in these studies the afterglow of the Cr$^{3+}$ luminescence was not desired and was intended to avoid, G. Blasce et al. demonstrated that in the X-ray-excited Gd$_2$Ga$_5$O$_{12}$:Cr$^{3+}$ phosphor the NIR afterglow could occur [11].

In our recent work, we found that Cr$^{3+}$-doped lanthanide gallogermanate garnet (La$_2$Ga$_3$Ge$_3$O$_{14}$:Cr$^{3+}$) phosphors fabricated by a solid-state reaction method can exhibit remarkable long-persistent phosphorescence in the NIR region, from about 660 nm to 1300 nm, with a persistence time of more than 1 h at room temperature. Our experiments also showed that the intensity and persistent time of the NIR phosphorescence can be further enhanced by co-doping a variety of other ions, such as Li$^+$, Zn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$ and Dy$^{3+}$, into the La$_2$Ga$_3$Ge$_3$O$_{14}$:Cr$^{3+}$ phosphor, probably due to the creation of more trapping centers for carriers in the phosphors [12]. In this contribution, we use Cr$^{3+}$ and Zn$^{2+}$ co-doped La$_2$Ga$_3$Ge$_3$O$_{14}$ phosphor as an example to introduce the NIR phosphorescence from Cr$^{3+}$ ions and discuss the related phosphorescence mechanisms. It is worth noting that while we are writing this paper, a similar lanthanide gallogermanate system was reported by Jia et al [13].

2. Experimental

The La$_2$Ga$_3$Ge$_3$O$_{14}$: 1 mole% Cr$^{3+}$, 1 mole% Zn$^{2+}$ (LGG:Cr,Zn) phosphor was fabricated by a solid-state reaction method. Stoichiometric La$_2$O$_3$, Ga$_2$O$_3$, GeO$_2$, Cr$_2$O$_3$, and ZnO powders with 1 mole% of B$_2$O$_3$ as a flux were mixed, ground, and then pre-sintered at 950 °C for 4 h in air. After ground again, the mixture was sintered at 1300 °C in air for another 4 h. The obtained phosphor exhibits light green body color and is pure La$_2$Ga$_3$Ge$_3$O$_{14}$ phase (JCPDS.
PDF #72-2464) as identified by X-ray diffraction. The fluorescence spectra and phosphorescence decay were measured at room-temperature using a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer equipped with a standard R928P photomultiplier tube (240–850 nm) and an extended, liquid nitrogen-cooled DSS-IGA020L InGaAs detector (800–1600 nm). All spectra were corrected for the optical system responses. The relative intensities of the spectra measured by the two detectors were compared by manual correction using a standard sample, so that a complete emission spectrum in the range of 550–1300 nm can be plotted. The irradiation sources for phosphorescence measurements include a 4-W 254 nm ultraviolet (UV) lamp and a 450-W Xenon lamp (240–800 nm) equipped in the Fluorolog-3 spectrofluorometer. Prior to the phosphorescence measurements, the sample was sufficiently exposed to irradiations for 10 min. Moreover, phosphorescence images of the phosphor at different time (e.g., 10 s and 100 s) after the stoppage of a UV lamp irradiation were taken using a digital camera via an ITT PVS-14 night vision monocular (with a GaAs photocathode) in a dark room.

3. Results and discussion

Figure 1(a) shows the normalized excitation and emission spectra of the LGG:Cr,Zn phosphor at room temperature. The shapes and positions of the emission bands vary with the excitation wavelengths. Under 254 nm excitation, there are two clear R lines (R1 line at 696 nm and R2 line at 688 nm from the Cr3+ 2E level) superimposing on a broad emission band peaked at 785 nm. Under 640 nm excitation, in contrast, a broadband emission peaked at 960 nm is obtained. The corresponding excitation spectra monitored at the R line and at the low energy emission band are also different in shapes and positions, as displayed in Fig. 1(a). The coexistence of the R lines and 785 nm emission band (assigned to 4T2 → 4A2 transition) suggests that part of Cr3+ ions locate in an intermediate field site in the LGG:Cr,Zn phosphor, which is similar to the case of β-Ga2O3:Cr3+ phosphor [14]. Meanwhile, in the Cr3+-doped gallogermanate system, the Cr3+ ions experience disorder-induced distributions of crystal field strengths [15–17]. Therefore, the broadband luminescence peaked at 960 nm (assigned to 3T2 → 4A2 transition) can be ascribed to the reduced site symmetry around some Cr3+ ions caused by the disorder [16,17]. The different luminescence channels are illustrated in Fig. 1(b) as a configurational coordinate diagram, in which the two solid line arrows and one dashed line arrow represent the emissions from the Cr3+ ions located in the intermediate and weak field sites, respectively.
In the LGG:Cr,Zn phosphor, the phosphorescence performances at different emission wavelengths are expected to be different because of the disordered Cr$^{3+}$ site distributions. However, the phosphorescence duration time measured at different emission wavelengths even by the same detector (say nothing of different detection systems, e.g., R928P photomultiplier tube and DSS-I1GA020L detector) cannot be directly compared because there usually present different spectral sensitivities. Using a night vision monocular, however, we can observe, monitor and record the Cr$^{3+}$-activated NIR phosphorescence, as well as qualitatively investigate the wavelength dependent phosphorescence when appropriate cut-off filters are used.

Figure 2 shows the phosphorescence images of LGG:Cr,Zn powder observed through 665 nm, 780 nm, and 830 nm cut-off filters at time of 10 s and 100 s after the stoppage of a 254 nm UV lamp irradiation in a dark room. The shallow regions in Fig. 2(a), 2(d) and 2(g) represent the detected phosphorescence wavelength ranges. The phosphorescence images in Fig. 2 show that after the 254 nm UV lamp irradiation the phosphorescence exists at any spectral ranges in the whole emission band. In all three scenarios, the emission intensities decrease gradually with the time and the emission can still be perceivable by the night vision monocular one hour after the irradiation.

Although the NIR fluorescence of the LGG:Cr,Zn phosphor can be effectively induced by a wide range of energies (as shown in Fig. 1), the situation for the NIR phosphorescence can be different because of the different activation mechanisms between the fluorescence and phosphorescence. To evaluate the effect of different excitation energies on the NIR phosphorescence, we study the phosphorescence characteristics of the LGG:Cr,Zn phosphor under the irradiation of a wide range of excitation energies (from UV to red) using the Fluorolog-3 spectrofluorometer.
Fig. 2. Detected phosphorescence wavelength ranges and NIR phosphorescence images of LGG:Cr,Zn powders observed through (a–c) 665 nm, (d–f) 780 nm, and (g–i) 830 nm cut-off filters at time of 10 s and 100 s after the stoppage of a 254 nm UV lamp irradiation in a dark room. The images were taken by a digital camera through a night vision monocular.

Figure 3(a) shows the phosphorescence decay curve of the LGG:Cr,Zn phosphor monitored at 740 nm after 10 min of 260 nm irradiation. The persistent emission can be detected for more than 1 h, which is consistent with the observation using the night vision monocular. The point of $I_{10s}$ represents the phosphorescence intensity recorded at time of 10 s after the stoppage of the irradiation.

In the evaluation of the excitation energy-phosphorescence relationship, the following two conditions were followed. (1) To avoid the influence of the fast early decay on the analysis of phosphorescence, the phosphorescence intensity values at the $I_{10s}$ points under different excitation energies were compared. (2) To all excitation energies, the phosphorescence was monitored at the same wavelength (740 nm in present study). This is because for the same persistent phosphor, a certain phosphorescence wavelength is supposed to correspond to particular emitting center and traps, which allows for fairly evaluating the effectiveness of different excitation energies. Figure 3(b) shows the $I_{10s}$ values monitored at 740 nm emission as a function of excitation energies. The fluorescence excitation spectrum monitored at 740 nm is also given in Fig. 3(b) for comparison. Regarding to the excitation spectrum, the high energy excitation band (from 240 to 300 nm) and the small band side (from 300 to 360 nm) on its shoulder can be assigned, respectively, to the $O\rightarrow Cr$ charge transfer band and the $^4A_2\rightarrow^4T_1(te^2)$ excitation band. Figure 3(b) clearly shows that the NIR phosphorescence can be effectively achieved under UV illumination (~240–360 nm) but is barely achieved by blue
light (~480 nm) irradiation. Furthermore, the fluorescence excitation energy peaked at around 600 nm is completely inactive to the NIR phosphorescence. Note that although the afterglow behaviors at different emission wavelengths may be different in the LGG:Cr,Zn system, the irradiation energy dependences of phosphorescence intensities monitored at different emission wavelengths, i.e., from 660 nm to 1300 nm, show the similar evolutions as that shown in Fig. 3(b).

Fig. 3. (a) Phosphorescence decay curve of LGG:Cr,Zn phosphor monitored at 740 nm after 10 min of 260 nm irradiation. The point of \( I_{10s} \) represents the phosphorescence intensity recorded at time of 10 s after the stoppage of the irradiation. (b) Phosphorescence intensity monitored at 740 nm emission as a function of irradiation energy (represented by balls) in LGG:Cr,Zn phosphor. The dashed line curve is the fluorescence excitation spectrum monitored at 740 nm.

Basing on the above experimental results, the phosphorescence mechanisms of the LGG:Cr,Zn phosphor under different irradiation energies are given below. Under UV irradiation, the ground state electrons of Cr\(^{3+}\) ions are promoted to the \( ^4T_1 (te^2) \) or some energy levels with higher energies. The excited electrons are trapped by the neighboring oxygen vacancies (\( V_O \)), which are close to the bottom of the conduction band and locate in the vicinity of the photogenerated Cr\(^{4+}\) ions. These trapped electrons are then thermally released to the photogenerated Cr\(^{4+}\) ions, leading to effective Cr\(^{3+}\) phosphorescence. For the case of blue light irradiation, the energy is perhaps too low to induce the above phosphorescence mechanism.
process. However, the blue light energy may activate the F centers (i.e., $\text{Cr}^{3+}e^-$) in the phosphor, which were found to exist in the lanthanum-based crystals [18]. Electrons are thermally released from the F centers to the neighbor traps at the $\text{Cr}^{4+}$ levels, leading to persistent emission of $\text{Cr}^{3+}$ ions.

The role of $\text{Zn}^{2+}$ in the phosphorescence process is unclear at present stage. The lower charged $\text{Zn}^{2+}$ cation may serve as charge compensation for the $\text{V}_0$ in the LGG:Cr,Zn system. The $\text{Zn}^{2+}$ dopant and $\text{V}_0$ may locate at the vicinity of the $\text{Cr}^{3+}$ dopant, resulting in the formation of defect clusters consisting of $\text{Cr}^{3+}$, $\text{V}_0$ and $\text{Zn}^{2+}$ in the LGG:Cr,Zn phosphor, which is similar to the case of $\text{Tb}^{3+}$-$\text{V}_0$-$\text{Ca}^{2+}$ clusters in the Lu$_2\text{O}_3$:$\text{Tb}^{3+}$,$\text{Ca}^{2+}$ phosphor [19]. This kinds of defect clusters can provide trapping centers for the electrons and thus enhance the phosphorescence of the LGG:Cr,Zn phosphor.

In summary, we have fabricated LGG:Cr,Zn NIR long-persistent phosphor with persistence time of more than 1 h and studied the NIR phosphorescence and its mechanisms under the irradiation of UV light and blue light. The NIR phosphorescence can be effectively achieved under UV illumination (~240–360 nm) but is barely achieved by blue light (~480 nm) irradiation, even though the blue light excitation are effective to the NIR fluorescence. The LGG:Cr,Zn NIR long-persistent phosphor may find applications in security, defense and bioimaging. Further work is needed to extend the $\text{Cr}^{3+}$-doped gallogermanate system by searching more suitable cations for both the host materials and co-dopants to achieve much intense and longer NIR phosphorescence.

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