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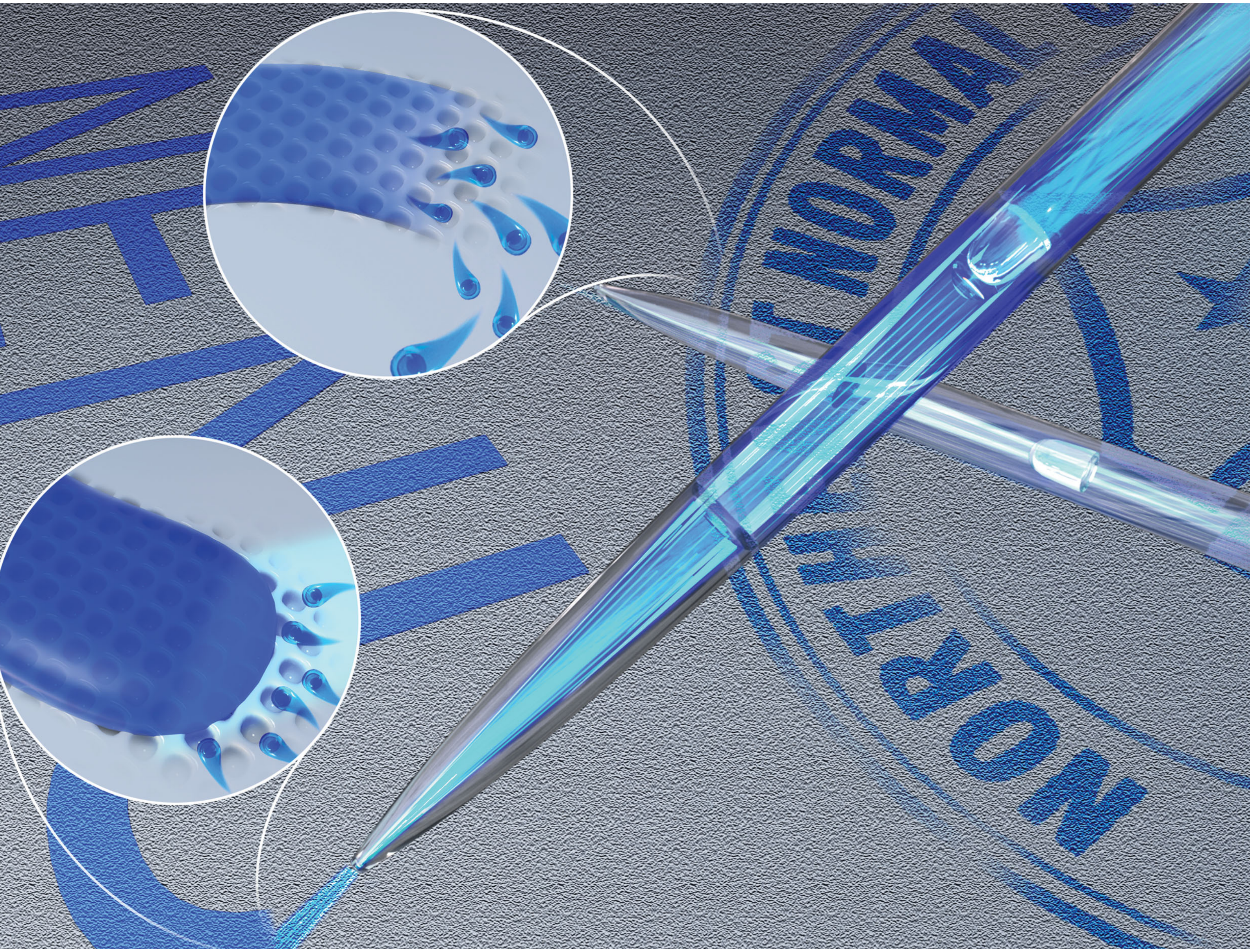

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Manipulating trap filling of persistent phosphors upon illumination by using a blue light-emitting diode†

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Developing a conceptual "write"/"read" technology for optical information storage of persistent phosphors is necessary but often underestimated. Here we demonstrate a "write"/"read" approach of traps upon illumination by using a blue light-emitting diode (LED) in persistent phosphors such as $LaMgGa_{11}O_{19}:Cr^{3+}$. Our investigation indicates that the phosphor can be charged upon high-power illumination (*e.g.*, incident power density of 0.5 W cm^{-2}) but discharged upon low-power illumination (*e.g.*, 0.1 W cm^{-2}). An appealing feature of the present approach is that the charging and discharging share the same illumination wavelength, which offers an interesting technical advantage and apparent convenience for applications. Moreover, such a manipulation technique is generally applicable for many existing phosphors.

Introduction

Persistent phosphors, which feature expected storage capability upon incident irradiation and controllable emission under external stimulation, can meet the requirements of some optical information storage techniques.[1–3] In the optical storage process of such phosphors, high-energy ionizing radiation (*e.g.*, high-energy ultraviolet light or X-ray) is generally employed to "write" information in the form of trapped electrons. Subsequently, the stored information can be "read" by low-energy illumination (*e.g.*, visible or infrared light) in the form of photostimulated luminescence or photostimulated persistent luminescence.[4–6] In the past few years, many research efforts have been devoted to optimizing the materials.[1–13] However, developing novel "write"/"read" technology for the optical information storage of persistent phosphors is often underestimated.

To write information into persistent phosphors, the constraint of high-energy excitability has been known for years, and thus some promising applications have been largely hindered.[14,15] As an alternative approach, an up-conversion charging (UCC) design,[16–19] which can effectively charge persistent phosphors using low-energy visible or infrared excitation sources, has offered a solution to the problem. In a UCC process, on one hand, the high-lying traps in persistent phosphors can be filled through a two-step photoionization of activator ions (*i.e.*, electron trapping process). On the other hand, while filling the traps, the external illumination may simultaneously promote some captured electrons from the traps to the delocalized continuum state of the phosphor (*i.e.*, photostimulated detrapping process).[19–21]

The relationship between the trapping and photostimulated detrapping of persistent phosphors can be described by a rate equation approach, in which we assume that the effect of retrapping is negligible. As illustrated in Fig. 1, during excitation, the rate equation is

$$\frac{dN_2}{dt} = N_1 \cdot A_1 - N_2 \cdot A_2, \tag{1}$$

where A_1 is the trapping rate, A_2 is the photostimulation detrapping rate, N_1 is the population of the UCC delocalized state, and N_2 is the electron population in the traps. Integrating eqn (1) gives

$$N_2 = \frac{N_1 \cdot A_1}{A_2} \pm \frac{C}{A_2} e^{-A_2 t}, \tag{2}$$

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† Electronic supplementary information (ESI) available: XRD pattern, illumination light path, decay curves, emission spectra after laser illumination, thermoluminescence curves, write/read of traps in LMG:Mn, and write/read of traps in LMG:Pr. See DOI: 10.1039/d0tc01427c

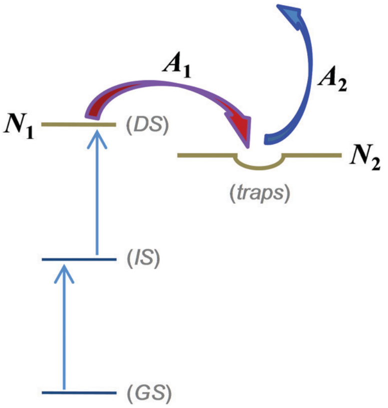

Fig. 1 Schematic illustration of electron trapping and photostimulated detrapping in an up-conversion charging (UCC) process upon illumination at power density *P*. The activator system is excited from the ground state (GS) to the UCC delocalized state (DS) *via* an intermediate state (IS). While the delocalized electron may be captured by the traps, the external illumination may simultaneously promote some of the captured electrons from the traps to the delocalized continuum state. Straight-line and curved-line arrows represent optical transitions and electron transfers, respectively. N_1 is the population of the UCC delocalized state, N_2 is the electron population in the traps, A_1 is the trapping rate, and A_2 is the photostimulated detrapping rate.

where *C* is a constant. Both the positive and negative solutions have their physical meaning. If $N_1{\cdot}A_1 - N_2{\cdot}A_2 > 0$ (corresponding to the negative solution), one can deduce that the population in the trap increases along with the illumination duration (*i.e.*, net filling of traps). In contrast, if $N_1{\cdot}A_1 - N_2{\cdot}A_2 < 0$ (corresponding to the positive solution), the population in the trap may decrease along with the illumination duration (*i.e.*, net releasing of traps). Such a competition between the trapping and detrapping inspires us to investigate the writing and reading performances of traps in persistent phosphors.

In this work, we carry out UCC investigations and demonstrate a new "write"/"read" approach of traps upon blue LED illumination on $LaMgGa_{11}O_{19}$ phosphors activated by Cr^{3+}, Mn^{2+} and Pr^{3+}. Here we use the newly developed $LaMgGa_{11}O_{19}$:Cr^{3+} phosphor as a representative material to experimentally reveal the competitive relationship between the electron trapping and photostimulated detrapping.

Experimental

Materials synthesis

The $LaMgGa_{11}O_{19}$:0.5%Cr^{3+} (LMG:Cr) phosphor was prepared by an usual solid-state technique. Starting materials, involving La_2O_3, MgO, Ga_2O_3 and Cr_2O_3 powders, were mixed in stoichiometric proportions. After being finely ground in an agate mortar for 3 h, the mixture was pressed into a disk of 1.5 cm in diameter. Subsequently, the disk was fired for 2 h at 1400 °C in air to obtain the resulting phosphor. The synthesized phosphor was confirmed to be single phase by X-ray diffraction using Cu Kα radiation (Fig. S1, ESI†). Other phosphors presented in the study, involving $LaMgGa_{11}O_{19}$:0.2%Mn^{2+} and $LaMgGa_{11}O_{19}$:0.5%Pr^{3+}, were also fabricated using the same method.

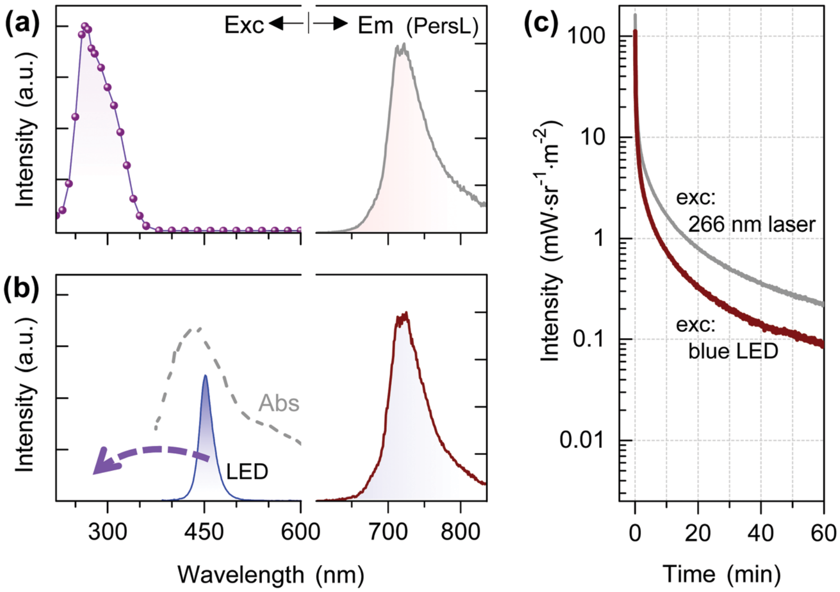

Fig. 2 Persistent luminescence of LMG:Cr phosphor. (a) Emission (right-hand side) and excitation (left-hand side) spectra for conventional persistent luminescence of the phosphor. The emission spectrum is recorded at 600 s after the stoppage of 266 nm laser illumination (0.5 W cm^{-2} for 1000 s). The excitation spectrum, which is an indication of delocalization energy for filling the traps, is obtained by plotting the persistent luminescence intensity as a function of the excitation wavelength. (b) UCC-induced persistent luminescence (UCC-PersL) emission spectrum recorded at 600 s after ceasing the blue LED illumination (0.5 W cm^{-2} for 1000 s). The left-hand side shows the output spectrum of the LED, as well as the diffuse reflectance absorption spectrum (Abs) of the phosphor over 380–600 nm. (c) Persistent luminescence decay curves after illumination with the 266 nm laser (0.5 W cm^{-2} for 1000 s) and the blue LED (0.5 W cm^{-2} for 1000 s).

Spectroscopic measurements

Persistent luminescence emission spectra were recorded with a Horiba FluoroMax-Plus spectrofluorometer. Persistent luminescence excitation spectra were recorded after illumination by various wavelengths of light from an Energetiq EQ-99XFC light source coupled with a Mini-Chrom monochromator (Edmund Optics, 190–650 nm). Persistent luminescence emission intensity (in units of mW sr^{-1} m^{-2}) was evaluated using a Thorlabs PM320E optical power meter equipped with a Thorlabs S130VC power sensor. Thermoluminescence measurements were conducted by a modified version of a SL08-L TL Reader (Guangzhou Rongfan Science and Technology Co., Ltd). The thermoluminescence curves were recorded for the Cr^{3+} emission with a heating rate of 4 °C s^{-1}. Before each measurement, the phosphor was heat-treated at 420 °C to empty all the traps. A high-power blue light-emitting diode (LED, LUMINUS-CBT-90TE-B, peak wavelength at 452 nm) served as the primary excitation source. The phosphor was illuminated by means of the blue LED light transmitted subsequently through a lens combination (Fig. S2, ESI†). The illumination light path allows us to focus the LED beam into a spot with a diameter of 1 cm. The illumination power density presented in this study is defined as the average power of the LED illumination beam reaching the surface of the phosphor divided by the beam area.

Results and discussion

The LMG:Cr phosphor exhibits persistent luminescence after charging by external illumination. As an example, Fig. 2(a) shows persistent luminescence emission and excitation spectra of the phosphor (see Fig. S3, ESI,† for details on the measurement of the excitation spectrum). After ultraviolet illumination with a 266 nm laser (0.5 W cm^{-2}) for 60 s, the phosphor gives rise to an asymmetric emission band with the intensity maximum at around 712 nm. Such an emission has been attributed to the transitions originating from the (Cr^{3+}) $^2\mathrm{E}$ and $^4\mathrm{T}_2$ states, as well as from Cr–Cr pairs.[22,23] The persistent luminescence excitation spectrum, which is an indication of delocalization energy for filling the traps,[15] is located in the ultraviolet region covering 220 to 360 nm.

Alternatively, the persistent luminescence of LMG:Cr phosphor can be achieved through a UCC approach. Such a charging process has been experimentally verified after illumination by various lasers, including a red diode laser, a green solid-state laser and a blue diode laser (Fig. S4, ESI†). According to previous studies,[16] the UCC-induced persistent luminescence of LMG:Cr can be described as follows. Upon excitation into the $^4\mathrm{T}_2$ or $^4\mathrm{T}_1$ level using the lasers, the Cr^{3+} ion relaxes rapidly to the intermediate states $^2\mathrm{E}/^4\mathrm{T}_2$. The excited electron in the intermediate states may be further promoted to a high-energy delocalized state, from where the electron is possibly captured by traps, followed by the delayed emission from the Cr^{3+} ion. Besides the excitations using lasers, considering the wide use of LEDs nowadays, here we use a convenient and low-cost blue LED as the excitation source to show the UCC capability of the phosphor.

Upon exposure to the blue LED illumination, as expected, the LMG:Cr phosphor shows effective persistent luminescence at room temperature. It is notable that the persistent luminescence excitation spectrum in Fig. 2(a) indicates that under linear excitation by the xenon arc lamp, the traps cannot be filled at the blue LED output wavelength. Thus, the achievement of persistent luminescence shown in Fig. 2(b) is unambiguously caused by the non-linear UCC mechanism. The persistent luminescence emission spectrum [right-hand side

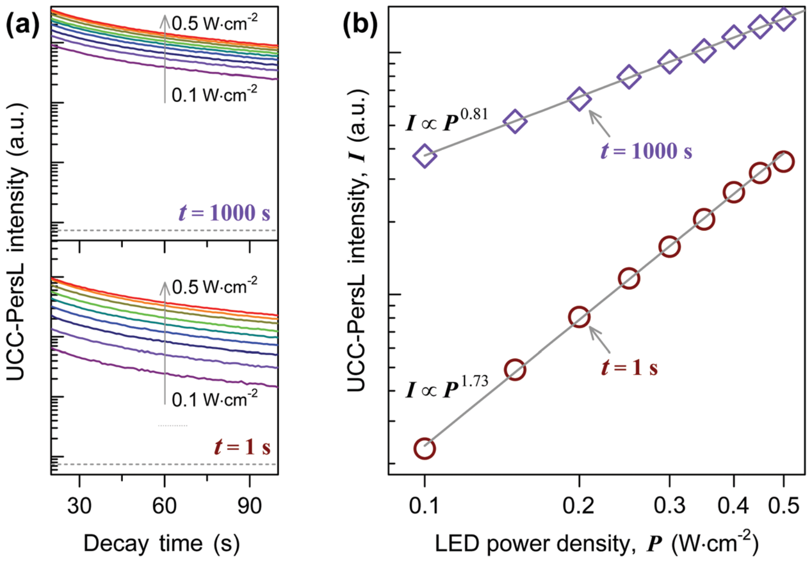

Fig. 3 Illumination power density dependence of UCC-PersL intensity of LMG:Cr for different exposure durations (t). (a) UCC-PersL decay curves recorded after ceasing blue LED illumination with different power densities from 0.1 to 0.5 W cm^{-2}. These curves are recorded by monitoring at 712 nm. The persistent luminescence intensity is obtained by integrating each curve over decay time. (b) Double logarithmic plots of the UCC-PersL intensity (I) *versus* the power density (P) of the blue LED. Exposure durations (t) are 1000 and 1 s, respectively.

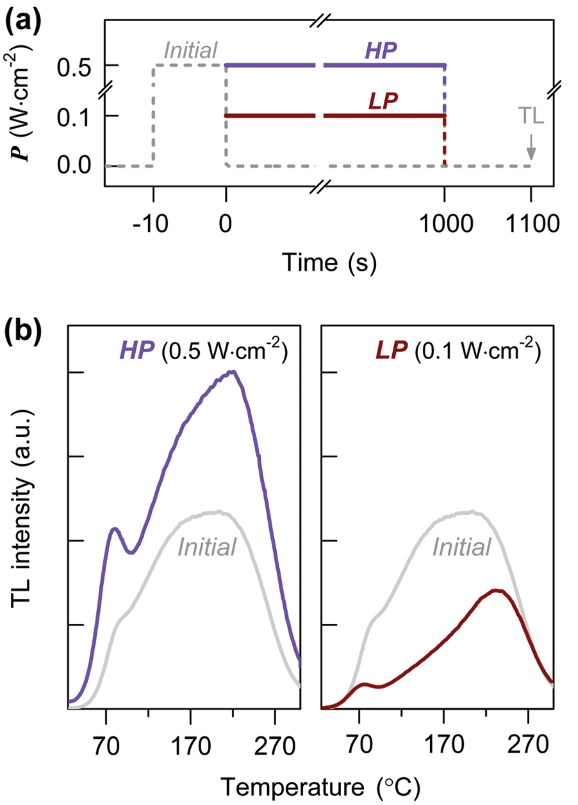

Fig. 4 Demonstration of optical writing and reading of traps upon illumination by the blue LED in LMG:Cr phosphor. (a) Designed experiment outline: the phosphor is initially illuminated for 10 s at 0.5 W cm^{-2} to fill some of the traps (initial illumination mode). Subsequently, LED secondary illumination with 0.5 W cm^{-2} (high power, HP mode) and 0.1 W cm^{-2} (low power, LP mode) is employed, respectively. Each secondary illumination ends at 1000 s and thermoluminescence (TL) measurement starts at 1100 s. (b) TL curves recorded after blue LED illumination with different illumination modes.

of Fig. 2(b)] has been recorded at 600 s after the illumination of the blue LED (0.5 W cm^{-2} for 60 s) has ceased. The emission shares a similar spectral profile to that of the conventional persistent luminescence emission shown in Fig. 2(a). The resulting UCC persistent luminescence intensities at 10 and 60 min delays are estimated to be 0.75 and 0.09 mW sr^{-1} m^{-2}, respectively [Fig. 2(c)].

For persistent phosphors, persistent luminescence performance generally depends on traps, while the integrated intensity of persistent luminescence decay is an indication of electron population in the traps. To verify the non-linear excitation process of the UCC in LMG:Cr, we investigate the illumination power density (P) dependence of the persistent luminescence emission intensity (I). For a sample with emptied traps (*i.e.*, $N_2 = 0$ at $t = 0$), eqn (2) can be written as

$$N_2 = \frac{N_1 \cdot A_1}{A_2}\left(1 - \mathrm{e}^{-A_2 t}\right). \qquad (3)$$

If the illumination duration is short enough ($\mathrm{e}^{-A_2 t} \approx 1 - A_2 t$), the electron population in the traps is proportional to the amount of delocalized electrons (*i.e.*, $N_2 \propto N_1$). Taking into account the features of up-conversion excitation,[24] we assume that $N_1 \propto P^n$ (n is the number of pump photons). Thus we can obtain $N_2 \propto P^n$. Accordingly, we have recorded the decay curves after the blue LED illumination with an exposure duration of 1 s at different power densities (0.1–0.5 W cm^{-2}), as presented in Fig. 3(a). Fig. 3(b) depicts the I–P function at a double-logarithmic coordination. As a consequence, a quadratic dependence $I \propto P^{1.73}$ is obtained by fitting the I–P plot, confirming that the trap filling is dominated by a two-photon excitation process. In addition, if the illumination duration is long enough ($\mathrm{e}^{-A_2 t} \approx 0$), then N_2 is given by $N_2 \propto N_1/A_2$ according to eqn (3). Taking into account the features of photostimulated detrapping,[20] we assume that $A_2 \propto P$. Thus we can obtain $N_2 \propto P^{n-1}$. This result is also consistent with our experimental result. As shown in Fig. 3(b), with a long exposure duration (*i.e.*, $t = 1000$ s), the intensity becomes linear with the LED power density ($I \propto P^{0.81}$).

Besides the persistent luminescence, the information related to the traps of persistent phosphors can also be provided by thermoluminescence measurements.[25–27] Accordingly, we have designed an extended thermoluminescence experiment to further evaluate the competition between the electron trapping and photostimulated detrapping in the UCC process of the LMG:Cr phosphor. As shown in the outline in Fig. 4(a), we will illuminate the phosphor using the blue LED with power densities of 0.5 and 0.1 W cm^{-2}, respectively, which are the maximum and minimum power densities presented in Fig. 3(b). Firstly, we illuminated the phosphor for 10 s using the blue LED (power density, 0.5 W cm^{-2}) to fill some of the traps (initial illumination mode). Subsequently, we illuminated the phosphor twice by combining the 10 s initial illumination and a secondary illumination, whose power density is fixed at 0.5 W cm^{-2} (high power, HP mode) or 0.1 W cm^{-2} (low power, LP mode). Both secondary illuminations ended at 1000 s, and the corresponding thermoluminescence measurements started at 1100 s.

Fig. 4(b) presents the thermoluminescence spectra of LMG:Cr recorded under different illumination modes by the blue LED. The spectra consist of two distinct broad bands peaking at 70 and 200 °C. Compared with the curve obtained under the initial illumination mode (grey curve), the HP mode resulted in a more intense thermoluminescence emission, indicating that the traps are being further written-in by the high-power LED illumination. The result is consistent with the negative solution of eqn (2). That is, the net effect of the HP mode is expected to charge the phosphor. In contrast, the LP mode resulted in a decrease of the thermoluminescence intensity. Such a result is consistent with the positive solution of eqn (2), implying that a net release of the partially filled traps proceeded under the LP mode. We therefore conclude that the net population in the traps can be manipulated by using the blue LED with different power densities. That is, the phosphor can be charged by high-power illumination and discharged by low-power illumination (Fig. S5, ESI†).

Besides the LaMgGa$_{11}$O$_{19}$:0.5%Cr^{3+} phosphor, we have also carried out investigations on the manipulations of trap filling in $LaMgGa_{11}O_{19}$:0.2%Mn^{2+} and $LaMgGa_{11}O_{19}$:0.5%Pr^{3+} (Fig. S6 and S7, ESI†). Both phosphors exhibit similar charging/discharging performance upon blue LED illumination. One can conclude that the net population in the traps of these phosphors can be adjusted upon LED illumination with different powers. Notably, the same illumination wavelength for the charging and discharging processes offers a unique technical advantage and apparent convenience for applications.

Conclusions

Using a blue LED as the excitation source, we have put forward and demonstrated a conceptually new approach for the optical "write"/"read" of traps in persistent phosphors. Our results have revealed that the net effect of high-power illumination contributes to the charging of phosphors (optical write-in). While a low power illumination, which shares the same blue LED output wavelength, may influence the trap population in a negative way (optical readout). Moreover, the manipulation of traps upon blue LED illumination is not an individual phenomenon, and can be achieved in different persistent phosphors. Consequently, our study presents a new perspective for understanding and predicting the trap filling of persistent phosphors. We therefore believe that our demonstration may offer some new opportunities for persistent phosphors in the field of optical storage.

Conflicts of interest

There are no conflicts to declare.

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