

# Potential white-light long-lasting phosphor: Dy<sup>3+</sup>-doped aluminate

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The white-light long-lasting phosphor CaAl<sub>2</sub>O<sub>4</sub>:Dy<sup>3+</sup> was prepared and investigated. The white-light afterglow spectra under the irradiation of 254 or 365 nm are comprised of the blue light emission and the yellow light emission, originating from the transitions of <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> in the 4f<sup>9</sup> configuration of Dy<sup>3+</sup>. The afterglow can last 32 min for the best sample with Dy-doped concentration of 2 at. %. The decay curve and the thermoluminescence curve show to be a second-order process. Thermoluminescence curves exhibit a complicated structure in the range of 230–450 K with the peaks at 244, 280, 310, and 346 K. The two thermoluminescence bands peaking above room temperature have corresponding traps with the depths of 0.54 and 0.61 eV, which are responsible for the afterglow emission at room temperature. This work provides a promising approach for the development of white-light long-lasting phosphor.  
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The long-lasting phosphors are a special kind of luminescent materials with long phosphorescence lasting for several hours at room temperature. In recent years, the long-lasting phosphors rare-earth-doped aluminates and silicates, such as aluminates SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup>,<sup>1–3</sup> CaAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Nd<sup>3+</sup>,<sup>4</sup> CaAl<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup>, Ce<sup>3+</sup>,<sup>5</sup> and silicates R<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>: (R=Ca, Sr, Ba)Eu<sup>2+</sup>, Dy<sup>3+</sup> (Ref. 6) have been proposed and developed because of their long duration, high luminosity, and improved chemical stability.

The colors of the developed long-lasting phosphors range from blue to red. For example, the SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> is an excellent blue long-lasting phosphor. Green, yellow, and red long-lasting phosphorescence was obtained in Mn<sup>2+</sup>-activated aluminate and silicate by Wang *et al.*<sup>7</sup> The afterglow color even can be specially designed according to the requirement of application using the concept of persistent energy transfer processes proposed by Jia *et al.*<sup>8</sup>

Unfortunately, no white-light long-lasting phosphor has been reported until now. Generally speaking, it is natural to consider that the white-light long-lasting phosphor can be achieved through the combination with the current available blue, green, and red phosphors according to appropriate ratio. However, this method is hard to work in practice since we can hardly ensure the very consistent afterglow decay process for the different components, thus resulting in the change in color with time. A more feasible approach is to find such a material that can produce white-light emission via the combination of different color emission from an identical luminescence center. The afterglow decay process is controlled by the properties of traps in the host. As a result, the different color emission from the identical center will have the same decay process, thus keeping the afterglow color unchanged.

Trivalent dysprosium with 4f<sup>9</sup> configuration has complicated energy levels and various possible transitions between *f* levels. The transitions between these *f* levels are highly selective and of sharp line spectra.<sup>9</sup> It is well known that

Dy<sup>3+</sup> has two intense fluorescence transitions from the <sup>4</sup>F<sub>9/2</sub> level to the <sup>6</sup>H<sub>15/2</sub> and <sup>6</sup>H<sub>13/2</sub> levels with the blue light emission at 477 nm and yellow light emission at 577 nm, respectively. The two color light emissions can produce white light through an appropriate combination. Therefore, Dy<sup>3+</sup> can be the appropriate luminescence center for us to develop the white-light long-lasting phosphors.

Recently, the long-lasting phosphorescence from Ce<sup>3+</sup> in the host of CaAl<sub>2</sub>O<sub>4</sub>, lasting up to 10 h, was observed.<sup>10</sup> The CaAl<sub>2</sub>O<sub>4</sub> is a suitable host for us to explore white-light long-lasting phosphor since defect-related traps can be easily formed when trivalent rare-earth ions are doped into such a host.

In this letter, we report some preliminary results on the white-light long-lasting phosphorescence from CaAl<sub>2</sub>O<sub>4</sub>:Dy<sup>3+</sup>. The traps responsible for the long-lasting phosphorescence are also studied using thermoluminescence technology.

The CaAl<sub>2</sub>O<sub>4</sub>:Dy<sup>3+</sup> powder samples with different doped concentration of 0.5, 1, 2, 4, and 8 at. % were prepared by high-temperature solid phase reaction using the raw CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and Dy<sub>2</sub>O<sub>3</sub> with the purity of 99.99%. The raw materials were mixed then sintered at 1350 °C for 8 h in air. All of the measurements except for the thermoluminescence curves were carried out at room temperature.

The excitation and emission spectra of CaAl<sub>2</sub>O<sub>4</sub>:Dy<sup>3+</sup> were measured with a Hitachi 850 fluorescence spectrophotometer and are shown in Fig. 1. All of the emissions observed are due to the 4f-4f transitions of Dy<sup>3+</sup>. Under the excitation at 349 nm, blue-light emission peaking at 477 and 491 nm and yellow-light emission peaking at 577 nm as well as a rather weak emission peaking at 668 nm were observed and can be assigned to the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub>, and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>11/2</sub> transitions of Dy<sup>3+</sup>, respectively. One can also find that the emission lines of Dy<sup>3+</sup> are broadened somewhat because there are several Stark levels for the <sup>4</sup>F<sub>9/2</sub> and <sup>6</sup>H<sub>*J*</sub> levels.<sup>11</sup> The sample with a Dy<sup>3+</sup>-doped concentration of 2 at. % has the strongest emission intensity. For most of the samples except for the Dy<sup>3+</sup> 0.5%-doped sample, the blue-

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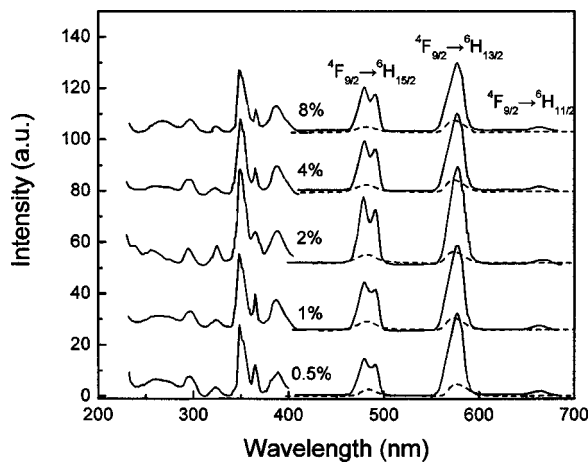


FIG. 1. Excitation ( $\lambda_{em}=577$  nm, left, solid lines), emission ( $\lambda_{ex}=349$  nm, right, solid lines), and afterglow (irradiation with 254 nm  $\sim 250$   $\mu\text{W}/\text{cm}^2$  for 10 min, right, dashed lines) spectra of  $\text{CaAl}_2\text{O}_4:\text{Dy}^{3+}$ .

light and the yellow-light emissions from  $\text{Dy}^{3+}$  can produce the white light for human eyes. While for the  $\text{Dy}^{3+}$  0.5%-doped sample, the yellow-light component is somewhat strong compared with the blue-light component, thus showing slight yellow light for the eye. This is because the yellow-light component with the transition of  ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$  is more sensitive to the crystal field environment. The excitation spectra with the emission at 577 nm consist of a series of line spectra in the 230–400 nm range with the strongest one at 349 nm and some lines at 256, 295, 325, 365, and 388 nm, which are ascribed to the transitions from the ground state to excitation states in the  $4f^9$  configuration of  $\text{Dy}^{3+}$  but not easy to be clearly assigned due to the dense and somewhat overlapped levels of  $4f$  configuration of  $\text{Dy}^{3+}$  in the high-energy region. The excitation with the wavelength shorter than 230 nm is involved in the interband transition of the  $\text{CaAl}_2\text{O}_4$  host whose band gap is about 5.78 eV derived from the photoconductivity spectra measurement.<sup>8</sup>

Since the monochromatic excitation light through a monochromator from the Xe lamp is not strong enough to create afterglow long enough for observation, we used the mercury lamps with 254 nm (low vapor pressure,  $\sim 250$   $\mu\text{W}/\text{cm}^2$ ) and 365 nm (high vapor pressure,  $\sim 50$   $\mu\text{W}/\text{cm}^2$ ) to irradiate the samples for the afterglow spectra, decay curves, and thermoluminescence curves measurements. The afterglow spectra after irradiated with 254 nm UV light for 10 min are shown in Fig. 1 (dashed lines). The measurement was performed 5 min after stopping the irradiation when the afterglow decay curves became flat in order to ensure that the spectrum shape did not distort so much. The afterglow spectra show same spectrum shape with the emission spectra.

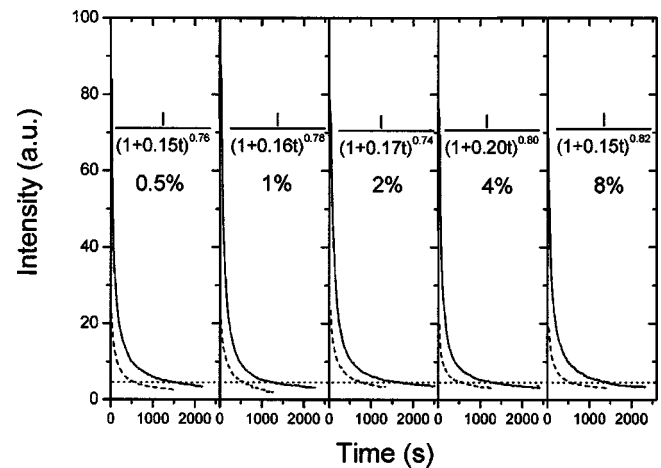


FIG. 2. Afterglow decay curves of  $\text{CaAl}_2\text{O}_4:\text{Dy}^{3+}$  after irradiation with 254 nm  $\sim 250$   $\mu\text{W}/\text{cm}^2$  for 10 min (solid lines) and with irradiation with 365 nm  $\sim 50$   $\mu\text{W}/\text{cm}^2$  for 10 min (dashed lines). The dotted line shows the limit of eye detection. The fitting formulas are for the curves after 254 nm irradiation.

Figure 2 shows the afterglow decay curves in spectral integral intensity after irradiation with 254 nm for 10 min (solid lines) and 365 nm for 10 min (dashed lines) for the five samples with different concentrations. In the dark, the afterglow emission from the best sample of  $\text{CaAl}_2\text{O}_4:\text{Dy}$  2 at. % is shown to be white light which can be observed by human eyes, lasting over 32 min, after irradiation with 254 nm UV for 10 min. The decay curve is well fitted by hyperbolic curve, indicating that the afterglow process meets a second-order mechanism.<sup>12</sup> The duration times for the different samples are summarized in Table I. The irradiation time of 10 min was enough. It was also found that increasing the irradiation time cannot significantly prolong the afterglow time. From Table I, one can find that the duration time of afterglow is dependent on the intensity of excitation source. After irradiation with 254 nm for  $\sim 250$   $\mu\text{W}/\text{cm}^2$ , the afterglow lasted over 25–32 min for different samples. In contrast to the case of 365 nm irradiation with  $\sim 50$   $\mu\text{W}/\text{cm}^2$ , the afterglow times of 10–13 min were obtained. This is reasonable because the afterglow intensity is dependent on the dose rate for the shallow traps.<sup>13</sup> The concentration of trapped electrons will attain an equilibrium value during irradiation. This value is expected to be proportional to dose rate.

The thermoluminescence curves are shown in Fig. 3. Several dominant peaks were observed at about 244, 280, 314, and 346 K, which are related to traps with different depth. Only these thermoluminescence bands peaking above room temperature are responsible for the afterglow at room

TABLE I. Afterglow duration time for the samples after irradiation by 254 and 365 nm.

	$\text{CaAl}_2\text{O}_4:$ Dy 0.5%	$\text{CaAl}_2\text{O}_4:$ Dy 1%	$\text{CaAl}_2\text{O}_4:$ Dy 2%	$\text{CaAl}_2\text{O}_4:$ Dy 4%	$\text{CaAl}_2\text{O}_4:$ Dy 8%
Duration of afterglow for eyes	(min)	(min)	(min)	(min)	(min)
After 254 nm ( $\sim 250$ $\mu\text{W}/\text{cm}^2$ ) irradiation for 10 min	29	28	32	25	27
After 365 nm ( $\sim 50$ $\mu\text{W}/\text{cm}^2$ ) irradiation for 10 min	10	11	13	10	10

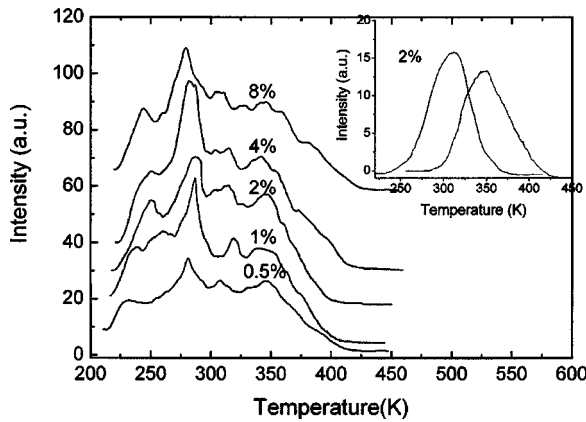


FIG. 3. Thermoluminescence of  $\text{CaAl}_2\text{O}_4:\text{Dy}^{3+}$  after irradiation with 254 nm for 10 min. The inset is the separated thermoluminescence bands of  $\text{CaAl}_2\text{O}_4:\text{Dy}^{3+}$  2 at. % for the peaks above room temperature. The heating rate is 0.2 K/s.

temperature. Therefore, we will focus on the thermoluminescence band peaking at 314 and 346 K for the  $\text{CaAl}_2\text{O}_4:\text{Dy}$  2% sample which has the longest afterglow. The thermoluminescence bands overlapped each other. In order to separate the overlapped thermoluminescence bands, a special method was applied. In this method, the irradiated sample was heated to about 320 K, thereby substantially emptying the traps responsible for the bands below 314 K. The sample was then rapidly cooled and reheated to 450 K, so the thermoluminescence curve consists of only 346 K band was obtained. Similarly, the thermoluminescence curve containing 314 and 346 K bands was also obtained. The latter curve was subtracted from the former curve, and then the thermoluminescence curve containing only 314 K band was obtained. The two separated thermoluminescence bands peaking at 310 and 348 K are shown in the inset of Fig. 3.

The symmetry of the two thermoluminescence curves suggest that we can process them using a second-order mechanism.<sup>14</sup> The depth of trap can be estimated by using an equation given by Chen *et al.*,<sup>15</sup>

$$E = 3.5(kT_m^2/\omega) - 2kT_m, \quad (1)$$

where  $T_m$  is the peak temperature,  $\omega$  is the full width at half maximum of the peak, and  $k$  is the Boltzmann constant.

The relationship between the frequency factor  $s$ , and the trap depth is given by

$$\beta E/kT_m^2 = s[1 + (b-1)2kT_m/E]\exp(-E/kT_m), \quad (2)$$

where  $\beta$  is the heating rate and  $b$  is 2 for the second-order process. The lifetime  $\tau$  of a trap with depth  $E$  at temperature  $T$  is given by

$$\tau = s^{-1} \exp(E/kT). \quad (3)$$

The trap parameters of depth  $E$ , frequency factor  $s$ , and the lifetime  $\tau$  at 300 K are calculated using the Eqs. (1)–(3) and listed in Table II.

$\text{Dy}^{3+}$  is an important rare-earth ion in the development of long-lasting phosphors, playing a crucial role. When the  $\text{Dy}^{3+}$  ions are codoped in the  $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$  phosphor, the afterglow time can be greatly prolonged and the afterglow

TABLE II. Trap parameters for  $\text{CaAl}_2\text{O}_4:\text{Dy}$  2%.

Peak temperature (K)	310	348
Trap depth $E$ (eV)	0.54	0.61
Frequency factor $s$ ( $\text{s}^{-1}$ )	$1.2 \times 10^7$	$1.7 \times 10^7$
Lifetime at 300 K (s)	209	2206

spectra is still due to the transition of  $5d \rightarrow 4f$  from  $\text{Eu}^{2+}$ . It is reasonable to consider that the role of doping  $\text{Dy}^{3+}$  ions is to introduce new types of traps or significantly increase the concentration of traps responsible for the afterglow. From the thermoluminescence curves with very complicated structure, one can believe that the types of traps are also very rich. We tentatively propose two possible types of the traps in  $\text{CaAl}_2\text{O}_4:\text{Dy}$ . In the first case, Dy ions act as not only luminescence centers but also traps, since Dy ions can form some electron trap levels in the band gap. In the other case, the traps can occur because of the charge compensation due to the substitution of trivalent  $\text{Dy}^{3+}$  ions for divalent  $\text{Ca}^{2+}$  ions in the host of  $\text{CaAl}_2\text{O}_4$ . The fact that the characteristic excitation of  $\text{Dy}^{3+}$  can lead to the afterglow emission from  $\text{Dy}^{3+}$  suggests that the trap filling process may occur through the direct transfer of electrons from the excitation states of  $\text{Dy}^{3+}$  to trap centers without via conduction band since the excitation energy is less than the band gap. During the afterglow emission, the trapped electrons are released and produce visible emission from  $\text{Dy}^{3+}$ .

In conclusion,  $\text{CaAl}_2\text{O}_4:\text{Dy}^{3+}$  exhibits white-light long-lasting afterglow which is due to the combination of blue and yellow light from the transitions between  $4f$  levels of  $\text{Dy}^{3+}$ . The afterglow can last over 32 min under the 254 nm irradiation and its decay process meets hyperbolic curve principle. The traps above room temperature have the depths of 0.54 and 0.61 eV, with the corresponding thermoluminescence peaks at 310 and 348 K, respectively. This is a potential white-light long-lasting phosphor although its afterglow requires it to be improved in terms of practical application.

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