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Photostimulated luminescence of $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} with a large energy storage capacity

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ABSTRACT

Strong and long-lasting photostimulated luminescence (PSL) is observed and studied in Eu^{2+} and Tm^{3+} codoped $Sr_3Al_2O_5Cl_2$ under 980 nm continuous stimulation after UV and blue light pre-irradiation. Compared to the Eu^{2+} singly doped one, the PSL intensity and energy storage capacity in the doubly doped material are enhanced by a factor of 400 and 91, respectively. The study indicates that codoping Tm^{3+} leads to a large increase of traps that enlarge energy storage capacity as three times as the commercial phosphor SrS:Eu^{2+}, Sm^{3+}.

1. Introduction

Photostimulated luminescence (PSL) material can store excitation energy by capturing charge carriers in traps when exposed to X-ray, ultraviolet light or visible light. The stored energy can be released by low-energy light (photon) stimulation, resulting in potostimulated emissions from the emitting centers in the phosphor. PSL materials have attracted much attention due to its significant application value in many aspects, such as infrared detection and optical information storage [1].

At present, the typical PSL materials contain alkaline earth metal halide (e.g., BaFBr and SrFCl) [2,3], alkali halide (e.g., KCl) [4] and alkaline earth metal sulfide (e.g., SrS and CaS) [5,6]. Among these materials, only alkaline earth metal sulfides exhibit photostimulating spectra in near the infrared region. However, the chemical and thermal stability of sulfides are poor, being not environment-friendly. Thus, it is necessary to search for new PSL materials that can be stimulated by infrared light with perfect chemical stability.

$Sr_3Al_2O_5Cl_2$:Eu^{2+} can be efficiently excited by ultraviolet (UV) and blue light, then emit in orange-yellow [7], is a potential phosphor for application in white light emitting diodes. Recently, Wang et al. reported that codoping Tm^{3+} in $Sr_3Al_2O_5Cl_2$:Eu^{2+} enables to generate a large number of traps and in turn achieve strong phosphorescence [8]. However, the photostimulated luminescence of $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} has not been demonstrated. The present paper demonstrates long lasting intense PSL phenomenon in $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} under 980 nm stimulation after the sample is irradiated by UV and blue light. Compared with the undoped Tm^{3+} sample, the PSL intensity and energy storage capacity of $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} are enhanced by a factor of 400 and 91, respectively. In particular, the energy storage capacity of $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} is three times as large as that of SrS:Eu^{2+}, Sm^{3+}. These results suggest that the $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} phosphor exhibiting PSL phenomenon can act as a novel candidate for optical information storage materials.

2. Experimental

Powder samples with nominal compositions of $(Sr_{2.99-x}Eu_{0.01})Al_2O_5Cl_2$:$x$Tm were synthesized by a high temperature solid state reaction at 1300 °C for 4 h in reductive atmosphere. The structure of sintered samples is identified by an X-ray powder diffractometer (Bruke D8 focus), operating at 40 kV and 40 mA using Cu Kα radiation ($\lambda = 1.54056$ Å) with a step size of 0.02° (2θ) in the range of 15–75°. The PL, PLE, PSL emission spectrum, PSL charging spectrum, TL curve and the decay curve of PSL were measured with a Hitachi F4500 spectrometer, which is equipped with a 150 W Xenon lamp under a PMT voltage of 700 V. And, the PL, PLE, and PSL charging spectra were corrected through multiplied by the correction curve. For PSL spectra and TL curves, in order to avoid the phosphorescence influences, the samples were pre-irradiated 5 min with appropriate wavelength and then placed in dark

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20 min before measurements. A 980 nm laser diode was used as an infrared stimulating light source. The TL curves were recorded with a heating rate of 0.3 K/s.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Sr_{2.99}Al_2O_5Cl_2$:0.01Eu^{2+} and $Sr_{2.983}Al_2O_5Cl_2$:0.01Eu^{2+}, 0.007Tm^{3+}. It can be observed that all of the peaks are in well agreement with JCPDS Card no. 80-0564. No other phase is detected, indicating that the obtained samples are single phase and the activator ions have been successfully incorporated in the host lattices.

Fig. 2(a) shows the PLE and PL spectra of $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+}, 0.007Tm^{3+} phosphor. The phosphor exhibits a typical orange-yellow emission band peaking at 600 nm. The PLE spectrum covers a broad spectral region from 200 nm to 500 nm, which is attributed to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} ions. Fig. 2(b) presents the PSL emission spectrum and PSL charging spectrum, which gives the initial intensity of the PSL as a function of the excitation wavelengths over the 200–500 nm spectral range in $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+}, 0.007Tm^{3+}. The PSL spectrum is almost identical to the PL spectrum, indicating that the PL and PSL spectra have the same emission centers. However, there is a little difference between the PLE and PSL charging spectra. In the PLE spectrum, the potoluminescence cannot be effectively excited by UV irradiation between 200–300 nm. While the PSL can be effectively achieved by a wide range of wavelengths (200–450 nm). The reason maybe that the energy of UV light in the 200–300 nm region is high enough to promote electrons in the conduction band and get trapped. Thus, it also can be observed a strong PSL phenomenon even if after 5 min irradiation by the UV light from 200 nm to 300 nm.

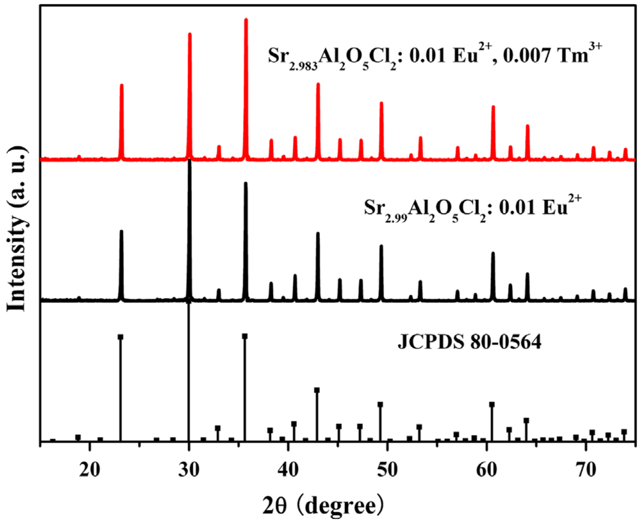

Fig. 1. XRD patterns of the $Sr_3Al_2O_5Cl_2$:Eu^{2+} and $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} phosphors.

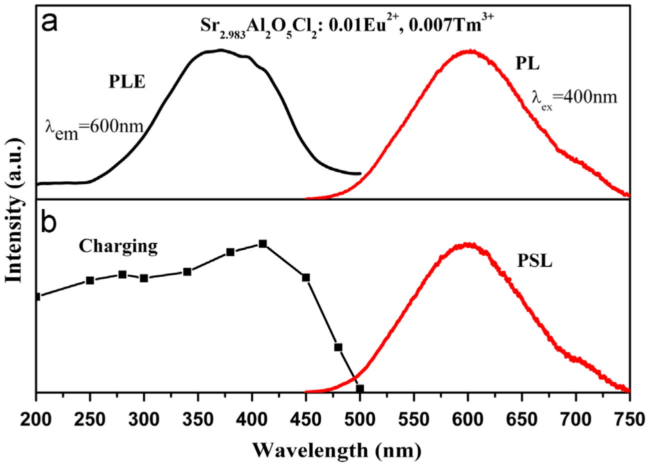

Fig. 2. PL and PLE spectra of $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+}, 0.007Tm^{3+} (a) and PSL emission spectrum and PSL response spectrum for charging wavelengths (b).

Fig. 3 shows the decay curves (monitored at 600 nm) of a series of $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+}, $x$$Tm^{3+}$ phosphors under continuous 980 nm laser stimulation. In measuring PSL decay curves, the samples were charged under the same condition. Compared to the Tm^{3+} free sample, the decay rate of the codoped Tm^{3+} samples become more slower in the first few seconds. With increasing the concentration of Tm^{3+}, the PSL intensities of $(Sr_{2.99-x}Eu_{0.01}Tm_x)Al_2O_5Cl_2$ phosphors enhance greatly, and the intensity reaches the maximum at the concentration of 0.007. It is well known that trapping centers play an essential role for energy storage in persistent, photostimulable, and thermostimulable phosphors. Therefore, it is possible speculated that with codoping Tm^{3+} into $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+}, the number of traps that have suitable depth which can be stimulated by 980 nm laser increase.

To verify this point of view, the TL spectra of $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+}, $x$$Tm^{3+}$ samples were measured. As shown in Fig. 4, there are at least three types of traps in the $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+}, $x$$Tm^{3+}$ phosphors for at least three peaks in the TL spectra, located at 60 °C, 130 °C and 305 °C. Addition of Tm^{3+} to $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+} results in a great enhancement of the three peaks compared with the undoped Tm^{3+} phosphor. Therefore, it can be concluded that doping Tm^{3+} into $Sr_3Al_2O_5Cl_2$:0.01Eu^{2+} phosphor does not induce new traps but only increase the number of the original three traps. The weak TL peaks of singly doped phosphor maybe originated from impurity Tm^{3+} in the process of sample

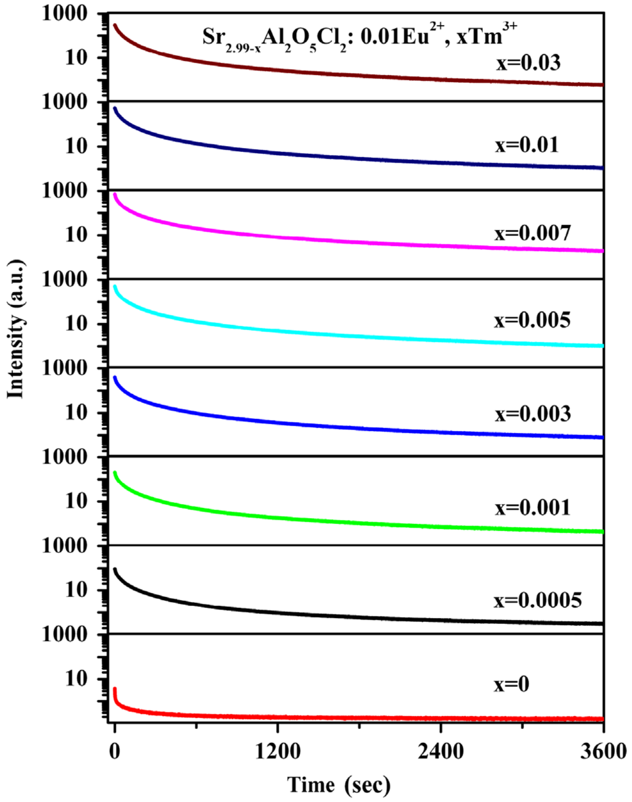

Fig. 3. The PSL decay curves of $Sr_{2.983}Al_2O_5Cl_2$:0.01Eu^{2+}, $x$$Tm^{3+}$ upon continuous stimulation of 980 nm infrared light with power density of 48.35 mW/cm^2.

preparation. The TL intensities enhance strongly with increasing Tm^{3+} concentration. The maximal TL intensity also occurs at the Tm^{3+} concentration of 0.007, implying the correlation with the PSL intensity.

In addition to PSL intensity, energy storage capacity is also an important factor for potostimulated luminescence. The energy storage capacity is generally in proportion to the area under the PSL decay curve (defined as PSL decay area). The relationship among TL intensity, PSL intensity and PSL decay area is shown in Fig. 5. The samples are labeled from 1 to 8 as the concentration of Tm^{3+} increases. It is observed that the variations of TL intensity, PSL intensity and PSL decay area keep consistent with the Tm^{3+} concentration increases from sample 1 to 8. From Table 1, it can be observed that the PSL intensity and the PSL decay area enhance more than 400 times and 91 times, respectively. The great enhancements are very significant for application in infrared detection.

PSL intensity decreases as the value of x beyond the optimal concentration. The possible reason is described as follows: when trivalent Tm^{3+} ions act as an auxiliary doped into the $\mathrm{Sr_3Al_2O_5Cl_2{:}0.01Eu^{2+}}$ phosphor, they would induce chemically nonequivalently substitutions to the Sr^{2+} sites. Due to these nonequivalent substitutions, an excess of positive charge in the lattice must be compensated. The possible approach to fulfill the charge compensation of the Tm^{3+} doped $\mathrm{Sr_3Al_2O_5Cl_2{:}0.01Eu^{2+}}$ phosphors is that two Tm^{3+} ions replace three Sr^{2+} ions to balance the charge of these phosphors, which create two $\mathrm{Tm}^{\cdot}_{\mathrm{Sr}}$ positive defects and one V'_{Sr} negative defect. The induced defects V'_{Sr} could act as quenching centers that generally reduce PSL intensity. Thus, for PSL decay curves, it is observed that the PSL intensities decrease as the concentration of Tm^{3+} beyond 0.007.

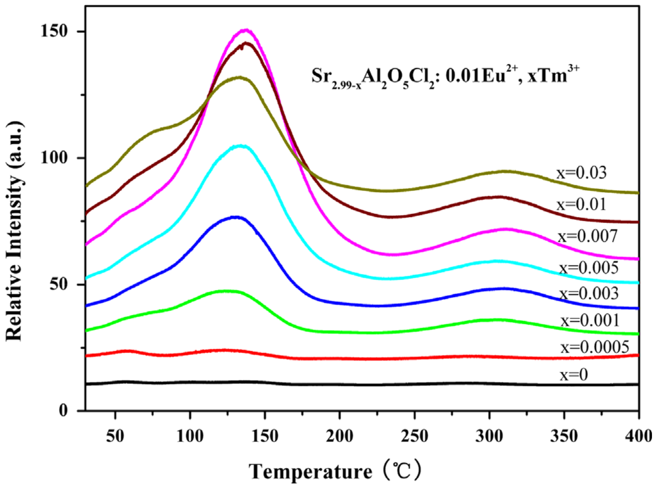

Fig. 4. Thermoluminescence (TL) patterns of $\mathrm{Sr_3Al_2O_5Cl_2{:}0.01Eu^{2+}}$, $x\mathrm{Tm}^{3+}$.

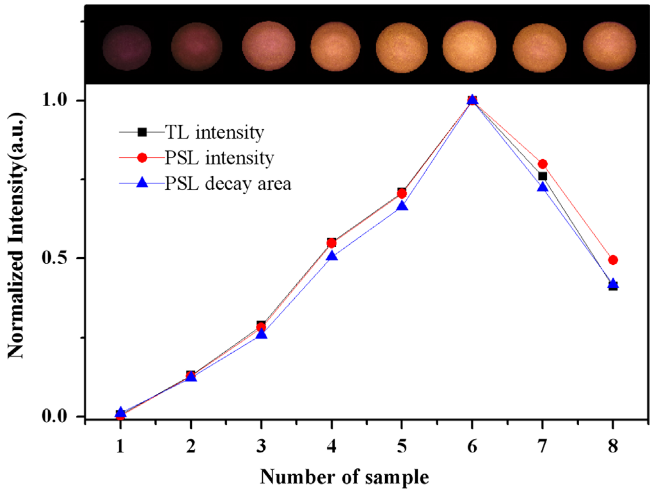

Fig. 5. TL intensity, PSL intensity and PSL decay area in $\mathrm{Sr_3Al_2O_5Cl_2{:}0.01Eu^{2+}}$, $x\mathrm{Tm}^{3+}$ from sample 1 to 8. Photographs are obtained under 980 nm excitation with power density 48.35 mW/cm^2.

The energy storage capacity of $\mathrm{Sr_3Al_2O_5Cl_2{:}0.01Eu^{2+}}$, $0.007\mathrm{Tm}^{3+}$ is two orders of magnitude larger than that of the Tm^{3+} free sample. In order to have a practical estimate of the energy storage capacity for $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} as a PSL material, its energy storage capacity has been compared with that of $\mathrm{SrS{:}Eu^{2+}}$, Sm^{3+}. Fig. 6 shows the PSL decay curve and PSL decay area of $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} compared with those of $\mathrm{SrS{:}Eu^{2+}}$, Sm^{3+} under the same optical power density. $\mathrm{SrS{:}Eu^{2+}}$, Sm^{3+} is excited by 460 nm and monitored the peak at 610 nm. The excitation wavelength of $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} is 400 nm and the monitored wavelength is 600 nm. As shown in Fig. 6, on the one hand, the PSL intensity of $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} decays much slower than $\mathrm{SrS{:}Eu^{2+}}$, Sm^{3+}. On the other hand, after 30 s under continuous infrared stimulating, the PSL intensity of $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} becomes higher than that of SrS: Eu^{2+}, Sm^{3+}. From the illustration in Fig. 6, it can be observed that the PSL decay area of $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} is three times larger than that of SrS: Eu^{2+}, Sm^{3+} (normalized for the PSL decay area of $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+}). Therefore, $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} has an excellent application in aspect of infrared detection.

4. Conclusion

In summary, we observed a strong orange-yellow PSL phenomenon under 980 nm stimulation in $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} after pre-exposure in UV-light. Tm^{3+} ions in the $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$ improve the electron-trapping ability of the samples, which make important contributions to the PSL phenomenon in this kind of

Table 1
PSL intensity and PSL decay area in $\mathrm{Sr_{2.983}Al_2O_5Cl_2{:}0.01Eu^{2+}}$, $x\mathrm{Tm}^{3+}$ (normalized to Tm^{3+} free sample).

Sample number	1	2	3	4	5	6	7	8
PSL intensity	1	56	124	242	311	441	325	218
PSL decay area	1	11	24	46	61	91	66	38

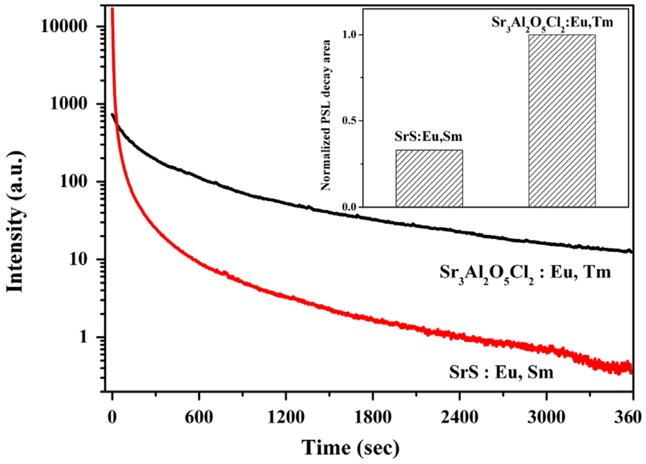

Fig. 6. The PSL decay curve of $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} compared with that of SrS: Eu^{2+}, Sm^{3+}. Inset: the comparison of PSL decay areas between $\mathrm{Sr_3Al_2O_5Cl_2{:}Eu^{2+}}$, Tm^{3+} and $\mathrm{SrS{:}Eu^{2+}}$, Sm^{3+}.

material. Compared with the Eu^{2+} singly doped phosphor, the PSL intensity and energy storage capacity of $Sr_3Al_2O_5Cl_2$:$0.01Eu^{2+}$, $0.007Tm^{3+}$ enhanced more than 400 times and 91 times, respectively. Especially, the energy storage capacity of $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} is three times as large as that of SrS:Eu^{2+}, Sm^{3+}. According to these results, $Sr_3Al_2O_5Cl_2$:Eu^{2+}, Tm^{3+} would be a new orange-yellow emitting PSL material for infrared detection.

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