Strongly enhancing photostimulated luminescence by doping Tm^{3+} in Sr_3SiO_5: Eu^{2+}

Xia Liu,[1,2] Jiahua Zhang,[1,*] Xia Zhang,[1] Zhendong Hao,[1] Jun Qiao,[1,2] and Xiaoling Dong[1,2]

[1]*State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Eastern South Lake Road, Changchun 130033, China*

[2]*University of Chinese Academy of Sciences, Beijing 100039, China*

**Corresponding author: zhangjh@ciomp.ac.cn*

Received November 16, 2012; revised December 13, 2012; accepted December 13, 2012;
posted December 14, 2012 (Doc. ID 180067); published January 9, 2013

We report a large enhancement of yellow photostimulated luminescence (PSL) by codoping Tm^{3+} in Sr_3SiO_5:Eu^{2+} upon infrared stimulation at 980 nm after pre-exposure in Ultraviolet light. The initial PSL intensity and light storage capacity are enhanced by a factor of 33 and 2, respectively, for Tm^{3+} concentration at 0.0004. The thermoluminescence spectra indicate that codoping Tm^{3+} generates a trap peaking at 385 K. The trap is much more sensitive to infrared light than the original one, so that the light storage period of the material is beyond tens of days with the minimum detectable infrared power density only 54 μW/cm^2. © 2013 Optical Society of America

OCIS codes: 160.2540, 300.2530, 160.2900, 160.2220.

Electron trapping materials (ETM) have been of great interest for their promising applications on infrared sensors, dosimeters, and near infrared to visible converters [1]. Electrons and holes can be trapped in ETM in charging processes by exposing them to ultraviolet (UV) or visible light, and subsequently can be released by infrared stimulation through recombining electrons and holes to generate visible photostimulated luminescence (PSL). Up to now, the commercial ETMs with the strongest PSL intensity and largest storage capacity have been alkaline sulfides, such as SrS: Eu, Sm [2], CaS: Eu, Sm [3]. However, they have poor chemical and thermal stabilities in air. In the past decades, many efforts have been made to search oxide ETMs for overcoming the drawback of sulfides. As we know, the phenomenon of PSL was observed in some oxide compounds, such as Sr_3SiO_5:Eu^{2+}, Dy^{3+} [4,5], $SrAl_2O_4$:Eu, Dy [6], and Mg_2SnO_4 [7]. Unfortunately, their PSL intensity and storage capacity must be enhanced substantially to meet applications.

Rare earth doped Sr_3SiO_5 is a well-known commercial phosphor that can efficiently absorb near-UV or blue-green light and emit in yellow for use in light-emitting diodes [8,9]. In our previous works, we have investigated the PSL properties in Sr_3SiO_5:Eu^{2+} and Sr_3SiO_5:Eu^{2+}, Dy^{3+} [4,5]. Regretfully, the PSL of them is not intense enough. In this Letter, we demonstrate a large enhancement of the yellow PSL by doping Tm^{3+} instead of Dy^{3+} to generate useful traps in Sr_3SiO_5:Eu^{2+}. The PSL intensity is enhanced 33 times compared with the Tm^{3+} free sample Sr_3SiO_5:Eu^{2+}.

The samples of $Sr_{2.99-x}SiO_5$:0.01Eu^{2+}, $x Tm^{3+}$ ($x = 0$, 0.00001, 0.0001, 0.0004, 0.001, 0.01, 0.04) are prepared by high temperature solid state reaction at 1400°C for 6 h. The photoluminescence (PL), photoluminescence excitation (PLE), thermoluminescence (TL), PSL, and PSL charging spectra, as well as the decay curve of PSL, are measured by using a Hitachi F4500 spectrometer. Before measuring the PSL, the samples were preirradiated by 330 nm UV light for 5 min and then placed in dark for 20 min. A 980 nm laser diode is used as a stimulating source. The TL is measured in the temperature range from 298 to 673 K with a heating rate of 0.3 K/s.

PL ($\lambda_{ex} = 470$ nm) and PLE ($\lambda_{em} = 580$ nm) spectra of $Sr_{2.99}SiO_5$:0.01Eu^{2+} and $Sr_{2.98}SiO_5$:0.01Eu^{2+}, 0.0004Tm^{3+} are displayed in Fig. 1. It is clearly shown that the PSL emission band is coincident with the PL band that peaks at 580 nm due to the electronic transition from the lowest lying $4f^6 5d^1$ to the ground state $4f^7$ of Eu^{2+}. However, an evident difference between the PLE and the PSL charging spectra is observed. The PLE spectra is composed of a group of UV bands and a blue-green band that are attributed to the transition from the ground state to the higher-lying $4f^6 5d^1$ and to the lowest lying $4f^6 5d^1$ of Eu^{2+}, respectively, while the PSL charging spectra is composed of only the group of UV bands, indicating that only UV light can be stored. As a result, it is speculated that the trap type for light storage in this material could be the electron trap. Upon UV exposure, only the electrons excited into higher $4f^6 5d^1$ states can be captured by traps below. If the traps are hole traps, the holes

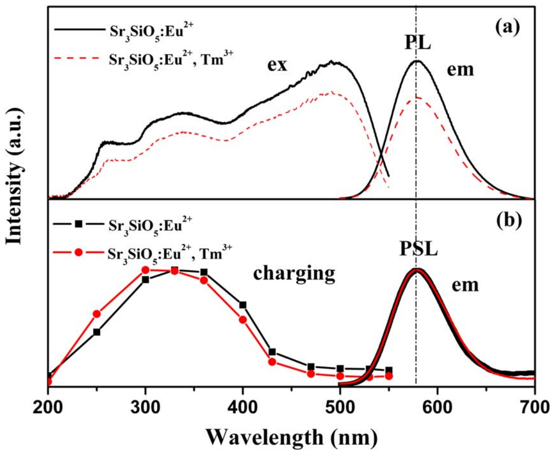

Fig. 1. (Color online) (a) PL and PLE spectra of $Sr_{2.99}SiO_5$:0.01Eu^{2+} and $Sr_{2.9896}SiO_5$:0.01Eu^{2+}, 0.0004Tm^{3+} and (b) PSL emission spectra and PSL response spectra for charging wavelengths.

0146-9592/13/020148-03$15.00/0

produced in the ground state of Eu^{2+} can enter the valence band of the host to fall into the hole traps. This process should not be influenced by the electrons either in higher or the lowest lying excited states of Eu^{2+}, implying PLE and PSL charging spectra are identical.

Figure 2 shows the PSL decay curves of $\mathrm{Sr}_{2.99-x}\mathrm{SiO}_5$:0.01$\mathrm{Eu}^{2+}$, $x\mathrm{Tm}^{3+}$ ($x = 0 \sim 0.04$). The significant results are described as below. On one hand, the initial PSL intensities enhance strongly as Tm^{3+} is codoped. The maximal intensity occurs at the Tm^{3+} concentration of 0.0004. On the other hand, the Tm^{3+} induced PSL exhibits a very fast decay compared to the original one. The decay rate of the fast component is two orders of magnitude faster than that of the original one. As a result, it is speculated that the doped Tm^{3+} ions could generate new traps that have big absorption cross sections for infrared light, which are more sensitive to infrared stimulation than the original traps that operate weak and slow PSL decay.

In order to confirm the existence of the new traps induced by Tm^{3+}, TL spectra of $\mathrm{Sr}_{2.99-x}\mathrm{SiO}_5$:0.01$\mathrm{Eu}^{2+}$, $x\mathrm{Tm}^{3+}$ ($x = 0 \sim 0.04$) are measured and shown in Fig. 3. There appear four peaks at 340, 385, 450, and 568 K that are labeled as A, B, C, and D, respectively. The measured peak temperatures of A, C, D in this work are all lower than that reported in our previous work [4,5], because here we use lower heating rate [10]. The remarkable growth of trap B with codoping Tm^{3+} is pronounced. The maximal TL intensity for trap B also occurs at Tm^{3+} concentration of 0.0004, implying the correlation with PSL. The identical intensity variation of PSL and peak B in TL with Tm^{3+} concentration is clearly shown in Fig. 4, where the samples are numbered from I to VII as the Tm^{3+} concentration increases. Accordingly, the enhancement of PSL is correlated to the generation of trap B. Figure 4 shows that the maximum PSL intensity is 33 times as large as that for the Tm^{3+}-free sample. The great enhancement is very crucial to application for infrared detection. The origin of trap B is still unclear at present; it may be Tm^{3+} itself or the point defect center induced by Tm^{3+}. The weak peak B for the Tm^{3+}-free sample shown in Fig. 3 is probably due to unintentional Tm^{3+} doping contained in $\mathrm{Eu}_2\mathrm{O}_3$ as the raw material for sample preparation.

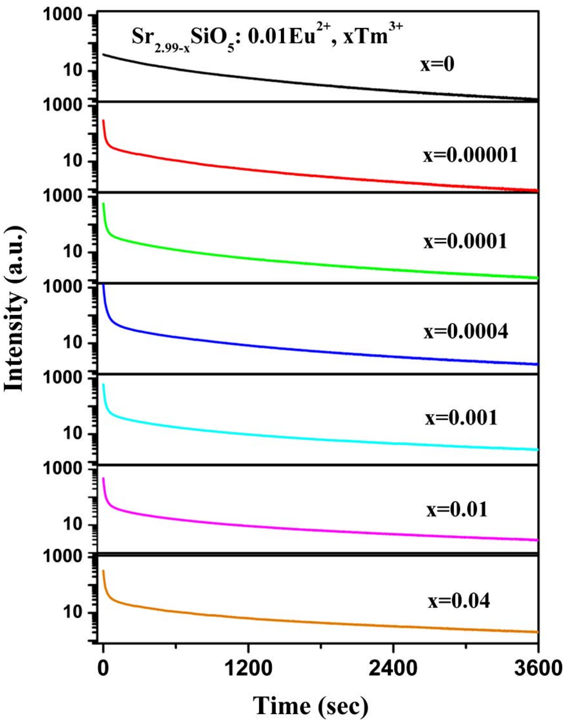

Fig. 2. (Color online) The decay curves of PSL in $\mathrm{Sr}_{2.99-x}\mathrm{SiO}_5$:0.01$\mathrm{Eu}^{2+}$, $x\mathrm{Tm}^{3+}$ ($x = 0 \sim 0.04$) monitored at 580 nm.

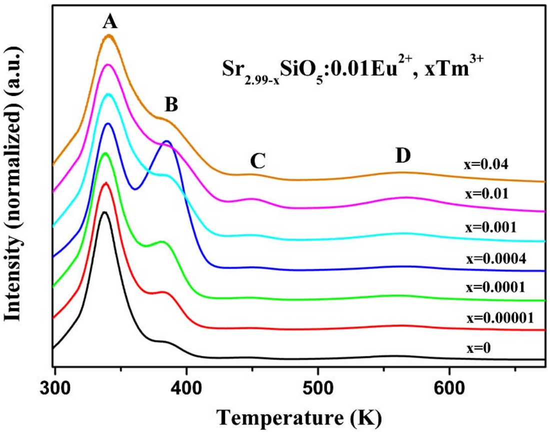

Fig. 3. (Color online) TL spectra of $\mathrm{Sr}_{2.99-x}\mathrm{SiO}_5$:0.01$\mathrm{Eu}^{2+}$, $x\mathrm{Tm}^{3+}$ ($x = 0 \sim 0.04$).

In view of the reduction of PSL for x larger than 0.0004, it is suggested that PSL mainly depends on evenly replacing of Sr^{2+} in the lattice position of $\mathrm{Sr}_3\mathrm{SiO}_5$ with Eu^{2+} and Tm^{3+}. Due to valence difference between Sr^{2+} and Tm^{3+}, defects such as Sr^{2+} vacancies are formed for charge compensation rather than interstitial O^{2-} that is large enough. On one hand, the number of trap B increases with increasing Tm^{3+} concentration. On the other hand, the increase of Tm^{3+} ions may simultaneously increase the number of defects such as Sr^{2+} vacancies. The induced defects could act as quenching centers that generally reduce PSL efficiency. Although the Tm^{3+} concentration of 0.0004 is quite low, the quenching could take place in the conduction band

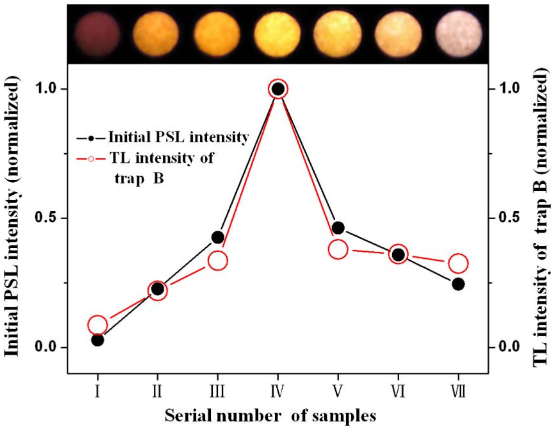

Fig. 4. (Color online) PSL and trap B TL intensities in samples $\mathrm{Sr}_{2.99-x}\mathrm{SiO}_5$:0.01$\mathrm{Eu}^{2+}$, $x\mathrm{Tm}^{3+}$ ($x = 0$, 0.00001, 0.0001, 0.0004, 0.001, 0.01, and 0.04) numbered from I to VII. Photographs are taken upon 980 nm stimulation with power density 15.27 $\mathrm{mW/cm}^2$.

Table 1. The Areas under PSL Decay Curves in $Sr_{2.99-x}SiO_5$:0.01Eu^{2+}, $x$$Tm^{3+}$ ($x = 0 \sim 0.04$)

x	Area (Normalized)
0	1.00
1.0×10^{-5}	1.05
1.0×10^{-4}	1.33
4.0×10^{-4}	2.05
1.0×10^{-3}	1.91
0.01	1.74
0.04	1.20

where electrons released from trap B have a long free path.

Total photons emitted in PSL refer to the light storage capacity, which is generally in proportion to the area under the PSL decay curve. The PSL areas (normalized to Tm^{3+} free sample) for various Tm^{3+} concentration are listed in Table 1. The maximum area also occurs at $x = 0.0004$, with the value twice that for the Tm^{3+}-free sample. In addition, the PSL can still be observed by naked eyes in $Sr_{2.9896}SiO_5$:0.01Eu^{2+}, 0.0004Tm^{3+} after 80 days storage in the dark at room temperature. The minimum detectable infrared power density is 54 $\mu W/cm^2$.

Another phenomenon with applied value we observed is partial recovery of PSL intensity after removal of infrared stimulation, as shown in Fig. 5. As the stimulation turns on again, the PSL intensity becomes stronger than that at the time stimulation was off. With increasing the time interval between stimulation off and on, the recovered PSL enhances. This result can be understood in terms of the effect of electron retrapping by trap B during the time interval when only thermally activated phosphorescence takes place. The thermally released electrons from the shallow trap A can be retrapped by deep trap B through the conduction band. Once the electrons are retrapped by trap B, they could be hardly released by heat at room temperature and consequently be accumulated and stored. As the stimulation-off period prolongs, more accumulation performs; hence, further enhancement of PSL intensity is expected. The time for retrapping is determined by the releasing time of trap A. It is observed that the phosphorescence takes 20 min to decay to 10% of its initial and can last 2 h at an intensity level recognizable by the human eye. In our previous works [4,5], only weak retrapping effect was observed in Sr_3SiO_5:Eu^{2+}, Dy^{3+}. The present work demonstrates a strong retrapping effect in Sr_3SiO_5:Eu^{2+}, Tm^{3+}, indicating the significant role of Tm^{3+} in producing trap B that is not only deeper than the original trap A, but also more sensitive to infrared light than trap A. Besides Dy^{3+}, in fact, we have researched the effects of all rare earths on intensity of PSL. Only Tm^{3+} shows remarkable production of a new trap B and the enhancement of PSL. The reason is still unclear at present. We suspect that it would relate to the unique electron configuration of Tm^{3+} that relates to trap B, which may well match the energy level structure of Eu^{2+} in Sr_3SiO_5.

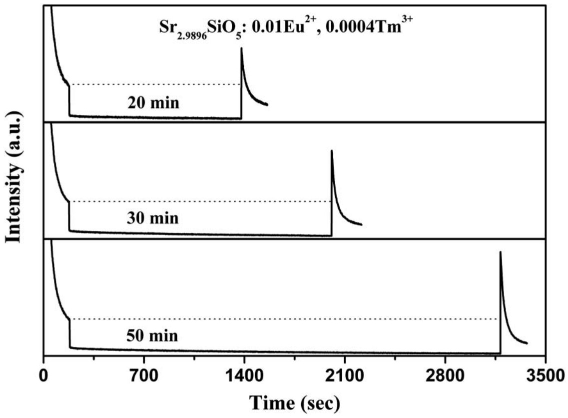

Fig. 5. The recovery of PSL intensity within different time intervals between infrared stimulation off and on in $Sr_{2.9896}SiO_5$:0.01Eu^{2+}, 0.0004Tm^{3+} (background is phosphorescence).

In summary, we have observed a large enhancement of yellow PSL by codoping Tm^{3+} in Sr_3SiO_5:Eu^{2+} upon infrared stimulation at 980 nm after being preirradiated by UV light. The initial PSL intensity and light storage capacity are enhanced by a factor of 33 and 2, respectively, for the sample $Sr_{2.9896}SiO_5$:0.01Eu^{2+}, 0.0004Tm^{3+}. A new trap with the TL peak at 385 K is produced by codoping Tm^{3+}. The new trap is much more sensitive to infrared light than the original one, leading to a minimum detectable infrared power density of only 54 $\mu W/cm^2$. The strong effect of retrapping by trap B is found as well. We offer a new oxide ETM exhibiting intense, yellow PSL, and high sensitivity to infrared light.

This work is supported by the National Natural Science Foundation of China (10834006, 51172226, 61275055, 10904141, 10904140) and National High Technology Research and Development Program of China (2010AA03A404).

References

1. J. Lindmayer, Solid. State Technol. **31**, 135 (1988).
2. L. H. Robins and J. A. Tuchman, Phys. Rev. B. **57**, 12094 (1998).
3. Z. Hasan, M. Solonenko, P. I. Macfarlane, L. Biyikli, V. K. Mathur, and F. A. Karwacki, Appl. Phys. Lett. **72**, 2373 (1998).
4. X. Y. Sun, J. H. Zhang, X. Zhang, Y. S. Luo, and X. J. Wang, J. Phys. D **41**, 195414 (2008).
5. X. Y. Sun, J. H. Zhang, X. Zhang, Y. S. Luo, Z. D. Hao, and X. J. Wang, J. Appl. Phys. **105**, 013501 (2009).
6. T. Katsumata, R. Sakai, S. Komuro, and T. Morikawa, J. Electrochem. Soc. **150**, H111 (2003).
7. J. C. Zhang, M. H. Yu, Q. S. Qin, H. L. Zhou, M. J. Zhou, X. H. Xu, and Y. H. Wang, J. Appl. Phys. **108**, 123518 (2010).
8. J. K. Park, C. H. Kim, S. H. Park, H. D. Park, and S. Y. Choi, Appl. Phys. Lett. **84**, 1647 (2004).
9. H. S. Jang and D. Y. Jeon, Opt. Lett. **32**, 3444 (2007).
10. R. Chen, J. Electrochem. Soc. **116**, 1254 (1969).