Journal of
Applied Physics

Effect of retrapping on photostimulated luminescence in Sr3SiO5:Eu2+, Dy3+ phosphor

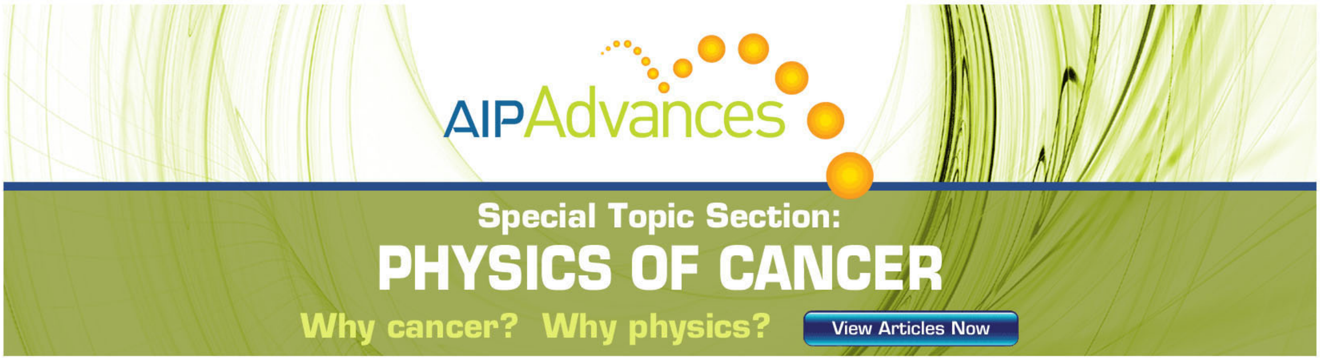
Xiaoyuan Sun, Jiahua Zhang, Xia Zhang, Yongshi Luo, Zhendong Hao et al.

Citation: J. Appl. Phys. **105**, 013501 (2009); doi: 10.1063/1.3050330

View online: http://dx.doi.org/10.1063/1.3050330

View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v105/i1

Published by the American Institute of Physics.



JOURNAL OF APPLIED PHYSICS **105**, 013501 (2009)

Effect of retrapping on photostimulated luminescence in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} phosphor

Xiaoyuan Sun,[1,2] Jiahua Zhang,[1,a)] Xia Zhang,[1] Yongshi Luo,[1] Zhendong Hao,[1] and Xiao-jun Wang[1,3]
[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, 16 Eastern South Lake Road, Changchun 130033, China*
[2]*Department of Physics, Changchun Normal University, Changchun 130032, China*
[3]*Department of Physics, Georgia Southern University, Statesboro, Georgia 30460, USA*

(Received 15 February 2008; accepted 6 November 2008; published online 5 January 2009)

$Sr_3SiO_5:Eu^{2+}$, Dy^{3+} exhibits a strong orange phosphorescence and photostimulated luminescence, originating from $4f^65d$-$4f^7$ transition of Eu^{2+}, after ultraviolet exposure. Shallow and deep traps are evidenced by thermoluminescence spectrum and decay curve of phosphorescence, which consists of a very fast and a slow component. The photostimulated luminescence presents a slow rising and a falling edge as an infrared excitation at 808 nm is turned on and off, respectively. This is attributed to the result of electron retrapping by shallow traps based on the analysis of dynamical process in photostimulated luminescence involved in photostimulated depopulation of deep traps. The electrons retrapped by deep traps is also demonstrated in the time interval between photostimulation off and on, which results in an enhanced rising edge relative to the former falling edge.
[DOI: 10.1063/1.3050330]

I. INTRODUCTION

Long phosphorescent materials have been of great interest due to the applications such as display devices, emergency illumination in dark environment, and optical storage.[1–6] Light energy can be stored in this kind material by exposing to radiation, x rays, ultraviolet (UV) or visible light, and subsequently released through thermal activation or photostimulation.[6–9] Up to the present, intense green and blue emitting persistent oxide phosphors have been commercially available with better chemical stability over sulfides.[1–5] Eu^{2+} and Dy^{3+} have been widely applied in many long phosphorescent hosts.[1,4,10,11] Eu^{2+}-doped Sr_3SiO_5 system produces a broadband emission peaked at 570 nm, which is a highly efficient orange emitting phosphor for white light emitting diodes.[12] Recently, we observed that $Sr_3SiO_5:Eu^{2+}$ also exhibits excellent characteristics of light energy storage to produce orange photostimulated luminescence (PSL) and long lasting phosphorescence. We also found that introduction of Dy^{3+} into $Sr_3SiO_5:Eu^{2+}$ can enhance PSL and prolong the phosphorescence as long as 6 h after UV irradiation.

When the electrons captured by traps are reactivated into the conduction band of a phosphorescent phosphor by thermal or photostimulation, they can be recaptured by traps before they are captured by an emitting center to cause phosphorescence. Retrapping is an important process in phosphorescent materials.[13,14] The decay curve of the phosphorescence is not generally represented by a simple exponential function due to retrapping.[14] PSL concerns electron releasing by photostimulation and electron retrapping, so that retrapping plays an important role on the properties of PSL. On this aspect, few investigations are demonstrated. In this paper, we investigated the effect of retrapping on PSL in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} phosphor. The PSL in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} presents a slow rising and a slow falling edge as the infrared excitation is turned on and off, respectively. The rising edges are higher than the former falling edges if the time interval between stimulation off and on is long enough. The experimental phenomena provide an evidence for the retrapping process in phosphorescent and PSL processes. PSL could be used as a probe to study retrapping process in phosphorescent materials.

II. EXPERIMENTAL

The phosphor $Sr_3SiO_5:0.01Eu^{2+}$, $0.03Dy^{3+}$ has been synthesized by the solid-state reaction technique. Eu^{2+} and Dy^{3+} substituted Sr^{2+} in the system. Stoichiometric mixtures of $SrCO_3$ (99%), SiO_2 (99%), Eu_2O_3 (99.99%), and Dy_2O_3 (99.99%) were ground together for 2 h, transferred to an alumina crucible, sintered in an electric furnace at 1300 °C for 4 h in a slightly reducing atmosphere (a mixture of 5% H_2 and 95% N_2), and cooled slowly to room temperature. The final phase was checked with a conventional x-ray diffraction (XRD) technique. Phosphorescence decay curve and PSL were measured with a Hitachi F-4500 spectral spectrophotometer. The thermoluminescence (TL) curve was recorded using a TL meter (model FJ-427A) with a heating rate of 5 K/s. The 808 nm laser radiation was produced with a laser diode.

III. RESULTS AND DISCUTION

A. XRD, phosphorescence, and TL

XRD pattern of $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} phosphor is shown as in Fig. 1. The pattern agrees well with the standard pattern of Sr_3SiO_5 available in Ref. 15, indicating that the phosphor synthesized are crystalline and single phase.

[a)] Author to whom correspondence should be addressed. Electronic mail: zhangjh@ciomp.ac.cn.

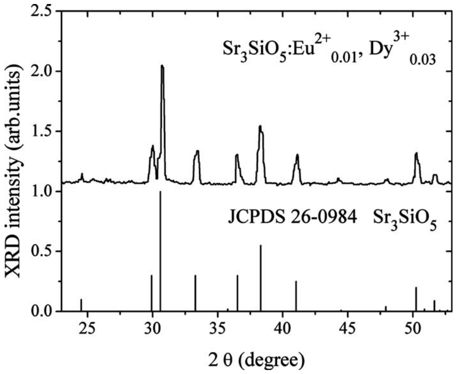


FIG. 1. XRD patterns of the $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} phosphor.

$Sr_3SiO_5:Eu^{2+}$, Dy^{3+} exhibits strong long orange phosphorescence, originating from $4f^65d$-$4f^7$ transition of Eu^{2+}, after UV exposure in the range of 200–400 nm. Figure 2 shows the decay curve of the orange phosphorescence in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} phosphor after UV irradiation at 370 nm. The phosphorescence spectrum is inserted in Fig. 2. The phosphorescence can last as long as 6 h. The decay pattern obviously consists of a fast component in the initial period of several seconds and a subsequently slow component as well as a very long decay tail after 1 h.

To understand the trap properties responsible for the phosphorescence, TL curve of $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} is measured after UV irradiation at 370 nm and illustrated in Fig. 3. Three TL peaks, A, B, and C, are detected, which are located at 369, 481, and 637 K, respectively.

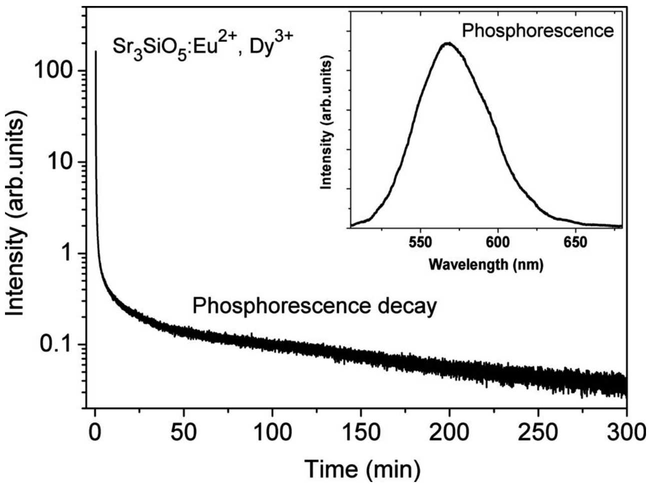


FIG. 2. The decay curve of the phosphorescence at 570 nm in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} phosphor. The phosphorescence spectrum is presented in the insert.

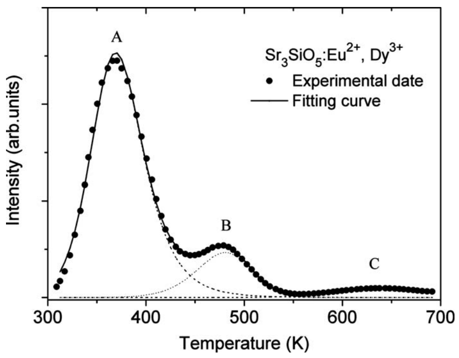


FIG. 3. Dots: TL curve of $Sr_3SiO_5:Eu^{2+}$, Dy^{3+}; solid line: the fitting curve.

Trap C, responsible for TL peak C, is not considered to be thermally released at room temperature to yield the phosphorescence because peak C occurs at a very high temperature around 637 K. Consequently, the slow phosphorescent component and the long tail are mainly attributed to the contribution of traps A and B, respectively. For the fast phosphorescent component, the responsible TL peak is not recorded in Fig. 3 because the fast component lasts only several seconds at room temperature shorter than the time separation between starting TL measurement and removal of UV exposure in this work. It can be speculated that the trap for the fast component is shallower than those traps A, B, and C. The TL parameters of thermal activation energy E (associated with the trap depth) could be obtained by fitting experimental data to the general order kinetics formula.[16,17] The TL intensity I as a function of temperature T is related via the following equation:[16,17]

$$I(T) = n_0 S \exp(-E/kT) / \left[1 + ((b-1)S/\beta) \times \int_{T_0}^{T} \exp(-E/kT)\, dT \right]^{b/(b-1)}$$

where n_0 is the concentration of trapped at $t=0$, k is Boltzmann's constant, β is the heating rate, E is the activation energy which means the trap depth, S is the frequency factor, and b is the order of kinetics. The TL is fitted well with the above equation, yielding the depths for traps A, B, and C to be 0.60, 0.80, and 1.09 eV, respectively. The obtained order of kinetics for traps A, B, and C are 2, 1.29, and 2, respectively, indicating that the phosphorescent dynamical processes in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} more fit the Garlick–Gibson model than Randall–Wilkens model.[18,19] The Garlick–Gibson model describes a second order kinetics in which retrapping is considered.

B. Retrapping in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+}

1. Retrapping by shallow traps

Upon infrared excitation at 808 nm, strong orange PSL is observed. The energy of an 808 nm photon is 1.53 eV; hence, the electrons even in the deepest trap C can be reactivated into the conduction band by 808 nm photons. An interesting phenomenon is that the PSL dose not cease promptly, but lasts several seconds after the termination of the infrared stimulation. To understand the dynamical process in PSL, the time response of PSL are studied as a weak infrared stimulation is turned on and off alternatively, as shown in Fig. 4. When the infrared stimulation is turned on, the PSL rapidly appears with an initial intensity and subsequently rises up until the maximum intensity is reached. When the infrared stimulation is turned off after the PSL reaches the maximum, the PSL rapidly falls down to an intensity and subsequently decays slowly. It is found that the decay pattern of the PSL is well consistent with the decay trace of the fast component in

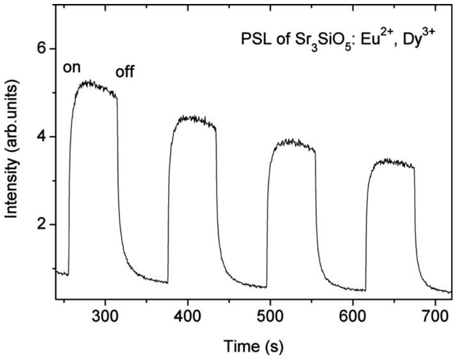


FIG. 4. The rising and falling edges of PSL (monitored at 570 nm) as the 808 nm excitation is turned on and off alternatively in Sr_3SiO_5:Eu^{2+}, Dy^{3+}. The decay of the phosphorescence is shown during the absence of the excitation.

phosphorescence, as shown in Fig. 5(a). These results demonstrate that the shallow traps for the fast component retrap electrons during the infrared stimulation in Sr_3SiO_5:Eu^{2+}, Dy^{3+}. Owing to very short persistence time of several seconds, the traps for the fast component should be close to empty before photostimulation. The electrons retrapped in the shallow traps come from the deep traps, such as traps A, B, and C, under photostimulation.

When the 808 nm photons excite electrons from various traps into the conduction band, a part of them recombine at luminescence centers, and the other recharge the shallow traps which are empty at the beginning of the photostimulation. With the recharging of the shallow traps, the recharging flux reduces, and consequently the PSL increases. Thus, a slow rising edge of PSL is presented after turning on the infrared stimulation. When the infrared stimulation is turned off, the recharged shallow traps thermally decay with time constant of several seconds. To simulate the rising and falling edges of the PSL, a simple model of PSL process in Sr_3SiO_5:Eu^{2+}, Dy^{3+} is proposed, as illustrated in Fig. 6. Light energy is stored in the traps by exposing to UV and subsequently reactivated into the conduction band through photostimulation or thermal activation. The electrons are recaptured by the traps or transited the conduction band to excited state level, and then recombined at ground state to cause phosphorescence.

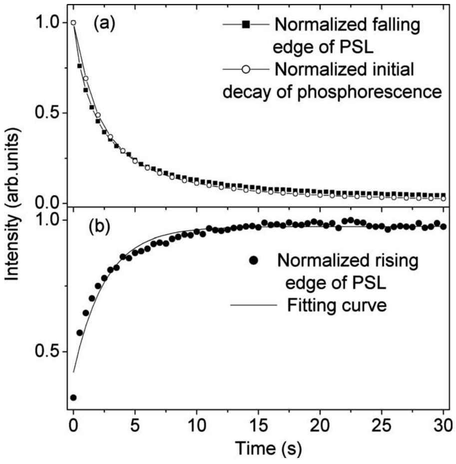


FIG. 5. (a) Comparison of the initial decay of phosphorescence and the falling edge of PSL (monitored at 570 nm). (b) Fitted the rising edge by using Eq. (4).

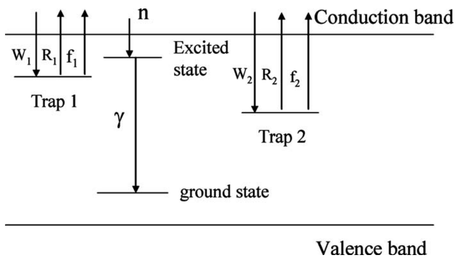


FIG. 6. A simple model of PSL process in Sr_3SiO_5:Eu^{2+}, Dy^{3+}.

Traps A, B, and C are classified as a deep trap denoted by trap 2 for simplicity. Let N_1 and N_2 be trap 1 and 2 numbers, and n_c, n_1, and n_2 the number of electrons in conduction band, and trap 1 and 2 states, respectively. The number of holes denoted by p is equal to $n_c+n_1+n_2$. The rate equations describing the PSL process are

$$\frac{dn_1}{dt} = -(R_1+f_1)n_1 + W_1 n_c (N_1 - n_1), \tag{1}$$

$$\frac{dn_2}{dt} = -(R_2+f_2)n_2 + W_2 n_c (N_2 - n_2), \tag{2}$$

$$\frac{dp}{dt} = -\gamma p n_c, \tag{3}$$

where R_1, R_2 are the thermal releasing rates for the trapped electrons in traps 1 and 2, respectively; f_1 and f_2 are the photostimulating rates for the trapped electrons in traps 1 and 2, respectively. The probabilities that a free electron in the conduction band will be captured by trap 1, trap 2, or to recombine with a hole are given by W_1, W_2, and γ, respectively. It is supposed that the number of the electrons n_c in the conduction band in the PSL process is so small that $p \approx n_1+n_2$ and $dp/dt \approx d(n_1+n_2)/dt$.

Due to short rising time and weak stimulation density, n_2 may be treated as a constant during the rising time. Due to rapid thermal releasing rate of trap 1, the case of $N_1 \gg n_1$, $n_2 \gg n_1$ is satisfied. Since the PSL intensity $I(t)=\gamma p n_c$, using Eqs. (1)–(3), we have

$$I(t)/I(\infty) = b\{1-\exp[-(1-b)(R_1+f_1)t]\} + 1 - b \tag{4}$$

for the rising edge profile, where $b=W_1N_1/[W_1N_1+W_2(N_2-n_2)+\gamma n_2]$ is the branch ratio of the depopulation rate for recharging the shallow traps to the total depopulation rates in conduction band.

Fitting the rising edge by Eq. (4), a rising time of 2.59 s and the branch ratio b of 57% are determined. The fitting curve is shown in Fig. 5(b).

Comparing the rising edge with the falling edge illustrated in Figs. 5(a) and 5(b), they have approximately the consistent time constant, indicating that R_1 governs the time constant rather than f_1 in the case of weak stimulation density.

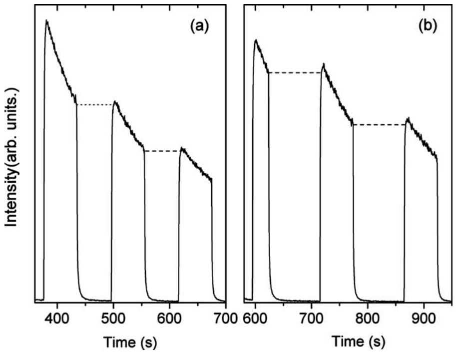


FIG. 7. Height of the rising and falling edges of PSL (monitored at 570 nm) as a strong 808 nm excitation is turned on and off alternatively with a different time interval in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+}. (a) The excitation interval is 60 s. (b) The excitation interval is 120 s.

2. Retrapping by deep traps

Figure 7 shows the rising and falling edges of PSL as a strong 808 nm excitation is turned on and off alternatively. It can be seen that the rising edge is higher than the former falling edge. When the time interval between stimulation off and on is increased from 60 s to 120 s, higher rising edge is achieved.

The results imply that the process of retrapping by deeper traps also occurs in the decay period of thermally activated phosphorescence stored in the shallower traps. For instance, once the electrons are retrapped by the deepest trap C, they cannot be thermally released at room temperature. The numbers of electrons in trap C, therefore, increase in the period of stimulation off. The longer period then further enhances the accumulation of electrons in trap C; hence, a higher rising edge relative to the former falling edge is expected.

It can be observed that the rising edge shown in Fig. 7 is sharper than that for weak stimulation, as shown in Fig. 4. This is because strong stimulation, on the one hand, remarkably increases the rate f_1, leading to reduction of rising time. On the other hand, strong stimulation speeds up depopulation of the electrons, n_2. In this case, the approximation of constant n_2 during rising process is failed.

IV. CONCLUSION

The effect of electrons retrapping on PSL is studied in $Sr_3SiO_5:Eu^{2+}$, Dy^{3+} phosphor. Electrons retrapped by shallow traps result in slow rising edges as the infrared excitation is turned on. The slow falling edges originate from the release of electrons retrapped by shallow traps. The enhanced rising edges relative to the former falling edges demonstrate that the electrons retrapped by deep traps occur in the time interval between photostimulation off and on. The results provide an evidence for the retrapping process in phosphorescent and PSL process. PSL could be used as a probe to study retrapping process in phosphorescent materials.

ACKNOWLEDGMENTS

The authors thank Dr. Chengyu Li for TL measurement. This work is financially supported by the MOST of China (2006CB601104 and 2006AA03A138) and by the National Science Foundation of China (10834006, 10774141, and 10574128).

[1] T. Matsuzawa, Y. Aoki, N. Takeuchi, and Y. Murayama, J. Electrochem. Soc. **143**, 2670 (1996).
[2] V. Abbruscato, J. Electrochem. Soc. **118**, 930 (1971).
[3] H. Yamamoto and T. Matsuzawa, J. Lumin. **72–74**, 287 (1997).
[4] Y. H. Lin, Z. L. Tang, Z. T. Zhang, and C. W. Nan, J. Alloys Compd. **348**, 76 (2003).
[5] N. Kodama, T. Takahashi, M. Yamaga, Y. Tanii, J. Qiu, and K. Hirao, Appl. Phys. Lett. **75**, 1715 (1999).
[6] V. G. Kravets, Opt. Mater. (Amsterdam, Neth.) **16**, 369 (2001).
[7] S. Jutamulia, G. M. Storti, J. Lindmayer, and W. Seiderman, Appl. Opt. **30**, 2879 (1990).
[8] J. Qiu, Y. Shimizugawa, Y. Iwabuchi, and K. Hirao, Appl. Phys. Lett. **71**, 759 (1997).
[9] J. Qiu, Y. Shimizugawa, Y. Iwabuchi, and K. Hirao, Appl. Phys. Lett. **71**, 44 (1997).
[10] M. Yamaga, Y. Masui, S. Sakuta, N. Kodama, and K. Kaminaga, Phys. Rev. B **71**, 205102 (2005).
[11] S. Ye, J. Zhang, X. Zhang, S. Lu, X. Ren, and X.-J. Wang, J. Appl. Phys. **101**, 063545 (2007).
[12] J. K. Park, C. H. Kim, S. H. Park, H. D. Park, and S. Y. Choi, Appl. Phys. Lett. **84**, 1647 (2004).
[13] E. Nakazawa, Y. Murazaki, and S. Saito, J. Appl. Phys. **100**, 113113 (2006).
[14] S. Shionoya and W. M. Yen, *Phosphors Handbook* (CRC, Boca Raton, FL, 1999), Chap. 2, p. 89–91.
[15] JCPDS No. 26-0984.
[16] R. Chen, J. Electrochem. Soc. **116**, 1254 (1969).
[17] S. W. S. McKeever, *Thermoluminescence of Solids* (Cambridge University Press, Cambridge, 1985), Chap. 3, p. 69.
[18] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. London **60**, 574 (1948).
[19] J. T. Randall and M. H. F. Wilkins, Proc. R. Soc. London, Ser. A **184**, 366 (1945).