Journal of Luminescence 148 (2014) 60–63

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Luminescence and energy transfer mechanism in $Sr_9Sc(PO_4)_7$: Ce^{3+}, Mn^{2+} phosphor

Xiaoling Dong [a,b], Jiahua Zhang [a,*], Xia Zhang [a], Zhendong Hao [a], Yongshi Luo [a]

[a] *Key Laboratory of Luminescence and Application, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 2 September 2013
Received in revised form
30 October 2013
Accepted 24 November 2013
Available online 4 December 2013

Keywords:
Phosphors
Luminescence
Energy transfer

ABSTRACT

A series of Ce^{3+} and Mn^{2+} co-doped $Sr_9Sc(PO_4)_7$ phosphors have been synthesized by high temperature solid state reaction and their luminescence properties are investigated. The obtained phosphors exhibit a broad excitation band ranging from 240 to 350 nm and two emission bands centered at about 370 and 610 nm upon 310 nm excitation, resulting from the 5d–4f transitions of Ce^{3+} and the d–d forbidden transition of Mn^{2+}, respectively. Energy transfer mechanism from Ce^{3+} to Mn^{2+} in $Sr_9Sc(PO_4)_7$ host matrix was studied and demonstrated to be a resonant type via a dipole–dipole mechanism based on the decay lifetime data. Furthermore, we have calculated the critical distance for $Ce^{3+} \rightarrow Mn^{2+}$ energy transfer to be about 6.12 Å by the spectral overlap method. Through effective energy transfer, a color-tunable emission varied from blue to reddish orange can be realized by adjusting the ratio of Ce^{3+} to Mn^{2+}. Our results indicate the novel $Sr_9Sc(PO_4)_7$: Ce^{3+}, Mn^{2+} phosphor can be a promising candidate for a color-tunable phosphor applied in a UV white light emitting diodes.

1. Introduction

Since Nakamura enabled technological access to blue light emitting diodes (LEDs), phosphor-converted white LEDs (pc-WLEDs) have brought a significant revolution in the field of illumination due to their superior characteristics over traditional light emitting devices. Many of the phosphors presently used are obtained by doping rare earth ions into host material. It is well known that Ce^{3+} activated phosphors show excellent luminescence efficiency due to the 5d–4f transitions. For example, the commonly used are down converting yellow emitting $Y_3Al_5O1_2$: Ce^{3+} phosphor and $Ca_3Sc_2Si_3O_{12}$: Ce^{3+} phosphors [1–3]. Moreover, Ce^{3+} ion can also act as an excellent sensitizer, transferring partial energy to activator ion such as Mn^{2+} [4–7]. As we have known, Mn^{2+} doped luminescent materials often show broad band emissions from 500 to 700 nm depending on the crystal field of the host materials [8–10]. However, the emission efficiency of Mn^{2+} is usually low as the d–d transition is difficult to be pumped in many hosts. Through codoping sensitizer, the Mn^{2+} emission can be realized efficiently by energy transfer, which plays an important role in development of efficient phosphor materials.

Phosphates are a type of promising host materials for their easy-synthesis, low-cost and chemical/thermal-stabilities over a wide range of temperatures. In this work, we have reported a novel $Sr_9Sc(PO_4)_7$: Ce^{3+}, Mn^{2+} phosphor. The energy transfer mechanism and critical distance (R_c) for energy transfer from sensitizer Ce^{3+} to activator Mn^{2+} have also been determined.

2. Experimental

The $Sr_{9-x}Sc_{0.85}(PO_4)_7$ (SSP): $0.15Ce^{3+}$, xMn^{2+} phosphors were synthesized by a high-temperature solid-state reaction. The constituent oxides or carbonates $SrCO_3$ (99.9%), Sc_2O_3 (99.9%), $(NH_4)_2HPO_4$ (99.9%), CeO_2 (99.99%), and $MnCO_3$ (99.99%) were employed as the raw materials, which were mixed homogeneously by an agate mortar for 30 min, placed in a crucible with a lid, and then sintered in a tubular furnace at 1400 °C for 4 h in reductive atmosphere (5% H_2+95% N_2 mixed flowing gas). Powder X-ray diffraction (XRD) data was collected using Cu-Kα radiation (λ=1.54056 Å) on a Bruker D8 Advance diffractometer equipped with a linear position-sensitive detector (PSD-50 m, M. Braun), operating at 40 kV and 40 mA with a step size of 0.01° (2θ) in the range of 15–55°. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Hitachi F7000 spectrometer equipped with a 150 W xenon lamp. The fluorescence decay curves of Ce^{3+} were measured by a FL920 Fluorescence Lifetime Spectrometer (Edinburgh Instruments, Livingston, UK) and a hydrogen flash lamp (nF900, Edinburgh Instruments). All the measurements were performed at room temperature.

---

* Corresponding author. Tel./fax: +86 431 88708875.
E-mail address: zhangjh@ciomp.ac.cn (J. Zhang).

0022-2313/$ - see front matter
http://dx.doi.org/10.1016/j.jlumin.2013.11.083

3. Result and discussion

3.1. Crystal structure

Fig. 1 shows the XRD patterns of the SSP: $0.15Ce^{3+}$ and SSP: $0.15Ce^{3+}$, $0.20Mn^{2+}$ samples. All the observed peaks are in good agreement with the standard data of $Sr_9Sc(PO_4)_7$ (JPCDS card no. 54-1186) and no other phase is detected. These results indicate that the obtained samples are single phase.

3.2. Photoluminescence properties of SSP: Ce^{3+}–Mn^{2+}

Fig. 2 presents the PL and PLE spectra of phosphor SSP singly and doubly doped with Ce^{3+} and Mn^{2+}. As shown in Fig. 2(a), the PL spectrum of SSP: $0.15Ce^{3+}$ displays a broad band extending from 330 to 450 nm, which attributed to the transition from 5d level to the ground state of Ce^{3+}. The excitation spectrum monitored at 370 nm shows a broad absorption band within the 240–350 nm UV range, originating from the 4f–5d transition of the Ce^{3+}. The emission and excitation spectra of a Mn^{2+} doped sample are shown in Fig. 2(b). SSP: $0.10Mn^{2+}$ phosphor presents a broad band peaked at 610 nm upon 404 nm excitation, which corresponds to the $^4T_1(^4G)\rightarrow{}^6A_1(^6S)$ transition of Mn^{2+}. The excitation spectrum of SSP: Mn^{2+} phosphor consists of several bands centered at 344, 355 and 404 nm, which are assigned to the transitions from $^6A_1(^6S)$ to $^4E(^4D)$, $^4T_2(^4D)$ and $[^4A^1(^4G), {}^4E(^4G)]$ levels of Mn^{2+}, respectively [11]. The emission intensity of Mn^{2+} are very weak at direct excitation of Mn^{2+} excitation levels due to the forbidden d–d transition of Mn^{2+}. In order to improve the emission intensity of Mn^{2+}, it is efficient to add sensitizer in the Mn^{2+} doped phosphors [12,13]. We have observed a significant spectral overlap between the Ce^{3+} PL and Mn^{2+} PLE spectra, indicating the possibility of energy transfer from Ce^{3+} to Mn^{2+} in SSP. The emission spectrum of Ce^{3+} and Mn^{2+} co-doped SSP is shown in Fig. 2(c), which includes not only a strong blue band from Ce^{3+} but also a strong red band from Mn^{2+}. It is found that the PLE spectrum monitored the red emission of Mn^{2+} is similar to that monitored the blue emission of Ce^{3+}, demonstrating effective energy transfer from Ce^{3+} to Mn^{2+} in SSP systems. Fig. 3 shows the emission spectra of Ce^{3+}, Mn^{2+} co-doped SSP with various Mn^{2+} concentrations, which were observed at an excitation wavelength of 310 nm. With the doping Mn^{2+} content increasing, the intensity of red emission at 610 nm increases systematically and reaches saturation when x is equal to about 0.20, whereas the intensity of the Ce^{3+} emission at 370 nm simultaneously decreases remarkably from $x=0$ to 0.30. These results also indicate the efficient energy transfer from the Ce^{3+} to Mn^{2+} ions. The emission intensity of the Mn^{2+} ions reach a maximum at $y=0.20$ and then begins to decrease due to the concentration quenching effect.

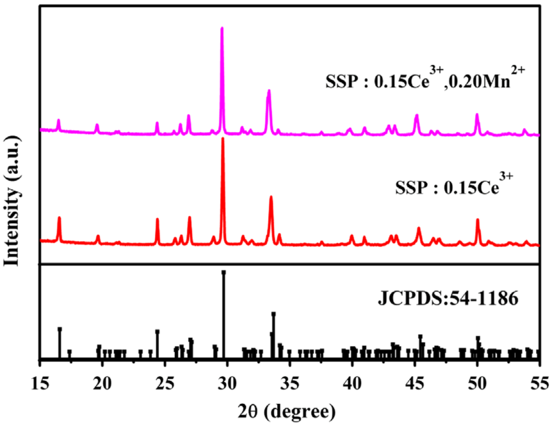

Fig. 1. XRD patterns of the $Sr_9Sc(PO_4)_7$: Ce^{3+} and $Sr_9Sc(PO_4)_7$: Ce^{3+}, Mn^{2+} phosphors.

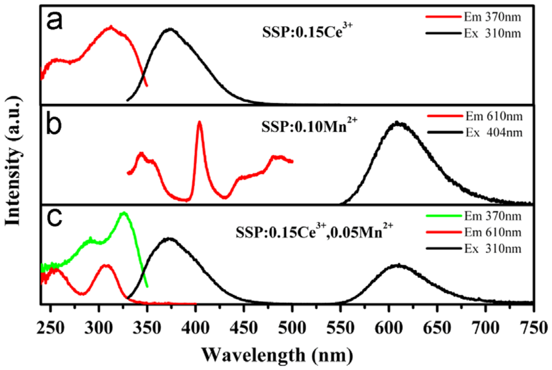

Fig. 2. PL and PLE spectra of $Sr_9Sc(PO_4)_7$: $0.15Ce^{3+}$(a), $Sr_9Sc(PO_4)_7$: $0.10Mn^{2+}$(b), and $Sr_9Sc(PO_4)_7$: $0.15Ce^{3+}$, $0.05Mn^{2+}$(c).

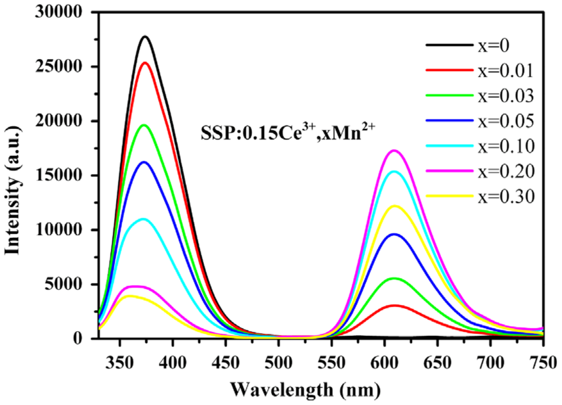

Fig. 3. PL($\lambda_{ex}=310$ nm) spectra of phosphors $Sr_9Sc(PO_4)_7$: $0.15Ce^{3+}$, xMn^{2+} with different Mn^{2+} contents.

The fluorescent decay curves of the Ce^{3+} ions in SSP: $0.15Ce^{3+}$, xMn^{2+} samples were measured by monitoring the emission of the Ce^{3+} ions at 370 nm as presented in Fig. 4. The values of the lifetimes are obtained by integrating the decay curves, of which the initial intensities are normalized. With increasing Mn^{2+} concentration, the fluorescence decreases and tends to be a nonexponential function, reflecting the characteristics of energy transfer between Ce^{3+} and Mn^{2+}. The energy transfer efficiencies (η) can be expressed by the following formula:

$$\eta=1-\tau/\tau_0 \tag{1}$$

where τ_o is the lifetime of the Ce^{3+} in the absence of the Mn^{2+} and τ is the lifetime of the Ce^{3+} in the presence of the Mn^{2+}. As a consequence, the η from Ce^{3+} to Mn^{2+} in SSP was calculated as a function of x and is represented in Fig. 4 inset. It is found that the values of η increase gradually with increasing Mn^{2+} contents and reaches 48% at $x=0.30$.

The decay curves in Fig. 4 change from exponential to non-exponential patterns with increasing x, reflecting the effect of energy transfer. If the donor and acceptor ions are uniformly distributed in the host, the migration process is negligible compared to energy transfer between donors and acceptors. The normalized intensity of the donor fluorescence can be written as

$$I_D(t)=I_{D0}(t)f(t) \tag{2}$$

where $I_{D0}(t)$ is the decay function of donors in the absence of acceptors and the function $f(t)$ characterizes the loss of excited donors due to one-way energy transfer to the acceptors. According

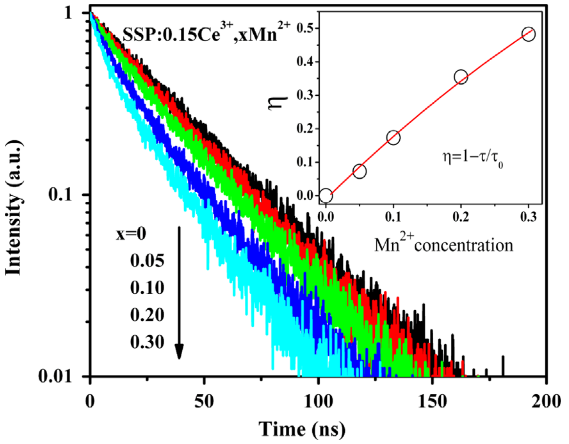

Fig. 4. Decay curves of Ce^{3+} fluorescence in SSP: $0.15Ce^{3+}$, xMn^{2+}(excited at 310 nm, monitored at 370 nm). Inset: energy-transfer efficiency with different doping Mn^{2+}contents.

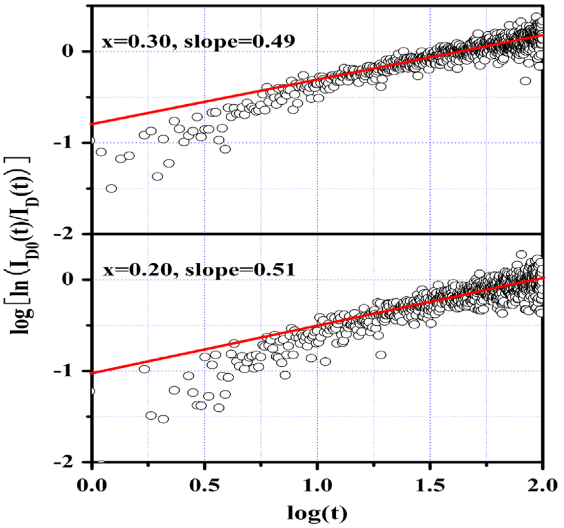

Fig. 5. Plotted $\log[\ln(I_{D0}(t)/I_D(t))]$ versus $\log(t)$ for SSP: $0.15Ce^{3+}$, xMn^{2+} phosphors.

to the Inokuti–Hirayama formula [14], we have

$$f(t) = \exp\left[-\frac{4}{3}\pi\Gamma\left(1-\frac{3}{m}\right)n_A\alpha^{3/m}t^{3/m}\right] \tag{3}$$

where α is a rate constant for energy transfer, $m=6$, 8, and 10 are the coefficients for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively, and n_A is the number of acceptor ions per unit volume. From Eqs. (2) and (3), $\log\{\ln[I_{D0}(t)/I_D(t)]\}$ acts as a linear function of $\log(t)$ with a slope of $3/m$. In order to well understand the Ce→Mn energy-transfer process, we plot $\log\{\ln[I_{D0}(t)/I_D(t)]\}$ versus $\log(t)$ for various samples, as shown in Fig. 5. The values of m estimated from the slope were found to be 5.88 and 6.12 for SSP: $0.15Ce^{3+}$, xMn^{2+} samples with $x=0.20$ and 0.30, respectively. The values are nearly coincident with the conventional value of $m=6$, indicating that the dominant interaction mechanism for SSP: Ce^{3+}, Mn^{2+} is based on the dipole–dipole interaction.

For the dipole–dipole interaction mechanism, the critical distance (R_c) for energy transfer from Ce^{3+} to Mn^{2+} can be obtained by the spectral overlap method [15]

$$R_c^6 = 3.024 \times 10^{12} f_d \int \frac{F_S(E)F_A(E)dE}{E^4} \tag{4}$$

where f_d is the oscillator strength of the involved absorption transition of the acceptor (Mn^{2+}), E is the energy involved in the transfer (in eV), and $\int F_S(E)F_A(E)dE/E^4$ represents the spectral overlap between the normalized shapes of the Ce^{3+} emission $F_S(E)$ and the Mn^{2+} excitation $F_A(E)$, and in our case, it is calculated to be about 0.0175 eV^{-5}. Using the above equation with $f_d=10^{-7}$ [16], the critical distance R_c was estimated to be 6.12 Å.

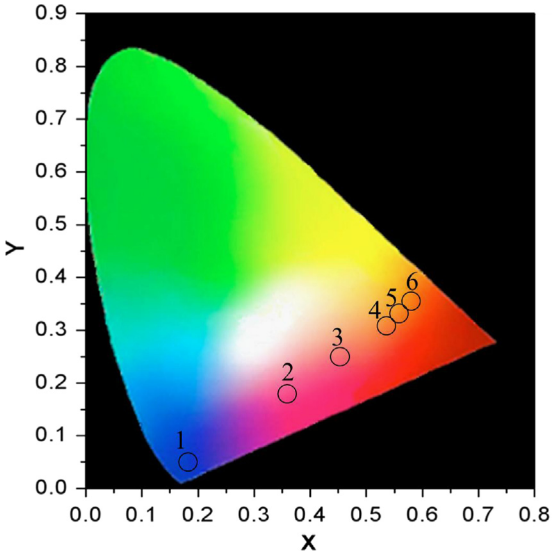

Fig. 6. CIE chromaticity diagram of $Sr_9Sc(PO_4)_7$: $0.15Ce^{3+}$, xMn^{2+} phosphors under 310 nm excitation. (1) $x=0$; (2) $x=0.01$; (3) $x=0.03$; (4) $x=0.05$; (5) $x=0.10$; and (6) $x=0.20$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The above results indicate that energy transfer between Ce^{3+} and Mn^{2+} exists in the phosphor SSP: $0.15Ce^{3+}$, xMn^{2+}, and the ratio between the blue emission and the red emission could be tuned by adjusting the concentration of Ce^{3+} and Mn^{2+}, respectively. The intensity ratio of blue and red affects the CIE chromaticity of phosphors, thus the effect of Mn^{2+} dopant contents on the CIE chromaticity coordinates is investigated in SSP: $0.15Ce^{3+}$, xMn^{2+} phosphors excited at 310 nm and the corresponding CIE are represented in Fig. 6. The color tone of the phosphors can be tuned from blue to reddish orange with the increase of the Mn^{2+} content from 0 to 0.30, and the corresponding CIE coordinates are calculated to change from (0.18, 0.05), (0.351, 0.180), (0.451, 0.255), (0.52, 0.31), (0.57, 0.35), (0.60, 0.37) to (0.60, 0.37). As the contents of Mn^{2+} beyond 0.20, the value CIE chromaticity of phosphor does not change remarkably, and this may be due to the effect of concentration quenching from Mn^{2+}.

4. Conclusion

In summary, a series of $Sr_9Sc(PO_4)_7$: Ce^{3+}, xMn^{2+} phosphor have been synthesized and investigated. The energy transfer from sensitizer Ce^{3+} to activator Mn^{2+} in $Sr_9Sc(PO_4)_7$ host has been studied and demonstrated to be a resonant type via a dipole–dipole mechanism. Furthermore, we have calculated the critical distance for $Ce^{3+} \rightarrow Mn^{2+}$ energy transfer to be about 6.12 Å. The emission color of the obtained phosphors can be easily modulated from blue to reddish orange by simply adjusting the amount of Mn^{2+} ions. These results indicated that $Sr_9Sc(PO_4)_7$: Ce^{3+}, Mn^{2+} may serve as a potential color-tunable UV phosphor for white-light LED devices.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (10834006, 51172226, 61275055, 11274007, and

11174278) and the Natural Science Foundation of Jilin Province (201205024).

References

[1] S. Nakamura, G. Fasol, The Blue Laser Diode, Springer, Berlin, 1997.
[2] Y. Shimomura, T. Honma, M. Shigeiwa, T. Akai, K. Okamoto, N. Kijima, J. Electrochem. Soc. 154 (2007) J35.
[3] Y.F. Liu, X. Zhang, Z.D. Hao, W. Lu, X.Y. Liu, X.J. Wang, J. Phys. D: Appl. Phys. 44 (2011) 075402.
[4] X.G. Zhang, M.L. Gong, Mater. Lett. 65 (2011) 1756.
[5] C.F. Guo, Y. Jie, X. Ding, M. Li, Z.Y. Ren, J.T. Bai, J. Electrochem. Soc. 158 (2) (2011) J42.
[6] G. Zhu, Y.H. Wang, Z.P. Ci, B.T. Liu, Y.R. Shi, S.Y. Xin, J. Electrochem. Soc. 158 (8) (2011) J236.
[7] Y.F. Liu, X. Zhang, Z.D. Hao, Y.S. Luo, X.J. Wang, J.H. Zhang, J. Mater. Chem. 21 (2011) 16379.
[8] M. Gu, L.C. Jia, X.L. Liu, S.M. Huang, B. Liu, C. Ni, J. Alloys Compd. 502 (2010) 190.
[9] E. Coetsee, J.J. Terblans, O.M. Ntwaeaborwa, H.C. Swart, Physica B 404 (2009) 4426.
[10] L. Shi, Y.L. Huang, H.J. Seo, J. Phys. Chem. A 114 (2010) 6927.
[11] W.J. Yang, L.Y. Luo, T.M. Chen, N.S. Wang, Chem. Mater. 17 (2005) 3883.
[12] A.H. Kitai, Solid State Luminescence, Theory, Materials and Devices, Chapman and Hall, London, 1993.
[13] Z. Hao, J. Zhang, X. Zhang, X. Sun, Y. Luo, S. Lu, X. Wang, Appl. Phys. Lett. 90 (2007) 261113.
[14] M. Inokuti, F. Hirayama, J. Chem. Phys. 43 (1978) 1965.
[15] G. Blasse, Philips Res. Rep. 24 (1969) 131.
[16] K.-S. Sohn, E.S. Park, C.H. Kim, H.D. Park, J. Electrochem. Soc. 147 (2000) 4368.