Available online at www.sciencedirect.com
ScienceDirect
Journal of Luminescence 128 (2008) 941–944
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Phase dependent photoluminescence and energy transfer in $Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} phosphors for white LEDs

Zhendong Hao[a,c], Jiahua Zhang[a,*], Xia Zhang[a], Shaozhe Lu[a], Yongshi Luo[a], Xinguang Ren[a], Xiaojun Wang[a,b,**]

[a]Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 Eastern South Lake Road, Changchun 130033, China
[b]Department of Physics, Georgia Southern University, Statesboro GA 30460, USA
[c]Graduate school of Chinese Academy of Sciences, Beijing, 100039, China

Available online 20 February 2008

Abstract

α- and β-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} phosphors were prepared by solid-state reaction. Phase transition from tetragonal (β-phase) to monoclinic (α-phase) is performed. A strong orange emission of Mn^{2+} is observed in both α-and β-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} upon near ultraviolet (UV) excitation through energy transfer from Eu^{2+} to Mn^{2+}. The transfer efficiencies for various Mn^{2+} concentrations are estimated based on lifetime measurements of the fluorescence of Eu^{2+} in the two phases. The photoluminescence excitation spectra of α-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} can cover 400 nm of the near-UV range, denoting its potential use as a phosphor with intense orange component for white light emitting diodes (LEDs).

Keywords: $Ca_2P_2O_7$; White LEDs; Energy transfer; Mn^{2+}; Phase transition; Eu^{2+}

1. Introduction

The white light-emitting diodes (LEDs) through combining blue LED (460 nm) with YAG: Ce^{3+} yellow phosphor and near-ultraviolet (UV) LED (400 nm) with tricolor phosphors have received increasing interest in recent years for its promising applications on solid state lighting [1,2]. The requirement of high color rendering index (CRI) need highly efficient orange or red phosphors for white LEDs.

The $Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} phosphor is a good phosphor for lamp through the energy transfer from Eu^{2+} to Mn^{2+} [3]. However, most of them concern beta phased $Ca_2P_2O_7$. In our previous work, we have prepared alpha phased $Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} phosphors in an attempt to find an orange phosphor suitable for near-UV LED [4]. In this paper, phase dependent photoluminescence and energy transfer in $Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} are comparably studied.

*Corresponding authors. Tel./fax: +86 431 86176317.
**Also to be corresponded to.
E-mail addresses: zhangjh@ciomp.ac.cn (J. Zhang), xwang@georgiasouthern.edu (X. Wang).

0022-2313/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2007.11.035

2. Experimental

The phosphors were prepared by solid-state reaction. The starting materials, analytical grade, were $CaHPO_4$, $(NH_4)_2HPO_4$, $MnCO_3$ and Eu_2O_3. Stoichiometric mixtures were homogenized and sintered at 600 °C for 1 h in air, cooled down, ground and sintered between 1150 °C and 1250 °C for 2 h in CO reducing atmosphere. The structures were identified by X-ray powder diffractometer (Rigaku D/M AX-2500 V). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by Hitachi F4500 spectrometer. In fluorescence lifetime measurements, a third harmonic (355 nm) of Nd-YAG laser (Spectra-Physics, GCR-130) was used as an excitation source, and the signals were detected with a Tektronix digital oscilloscope (TDS-3052).

3. Results and discussion

In Fig. 1, the XRD patterns of $Ca_2P_2O_7$: $0.01Eu^{2+}$, $0.10Mn^{2+}$, sintered at temperatures from 1100 °C to

1250 °C, exhibit an evolution of the tetragonal (β form) to monoclinic (α form) phase transformation. As sintered temperature is lower than 1150 °C, pure β-$Ca_2P_2O_7$ is obtained corresponding to JCPDS No.09-0346 which crystallizes in tetragonal space group of $P4_1$ with non-crystallographic symmetry [5]. As the sintered temperature is over 1200 °C, α-$Ca_2P_2O_7$ is formed and becomes dominant at 1250 °C, which crystallizes in monoclinic space group of $P2_1/n$ corresponding to JCPDS No.09-0345 [6].

Fig. 2 illustrates the PL spectra of $Ca_2P_2O_7$: 0.01Eu^{2+}, 0.10Mn^{2+} phosphor. All the PL spectra under 330 nm excitation show a blue emission band and an orange emission band, which are originated from 5d-4f transition of Eu^{2+} and $^4T_1(^4G)$-$^6A_1(^6S)$ transition of Mn^{2+}, respectively. Both Eu^{2+} and Mn^{2+} substitute for Ca^{2+} sites. With the phase transformation from β to α, it is observed that the blue band of Eu^{2+} slightly shifts from 419 to 414 nm while the orange band clearly shifts from 567 to 595 nm, of which the PLE spectra are shown in Fig. 3. It can be seen that the PLE band of Mn^{2+} in α-$Ca_2P_2O_7$: 0.01Eu^{2+}, 0.10Mn^{2+} is stronger than that in β-$Ca_2P_2O_7$: 0.01Eu^{2+}, 0.10Mn^{2+} at near-UV region of 400 nm, indicating that α-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} phosphor can be a good candidate orange phosphor for near-UV chip white LEDs. The PLE spectrum of Mn^{2+} singly-doped $Ca_2P_2O_7$ is also presented in Fig. 3 which peaks at 355 and 406 nm, corresponding to the forbidden transitions from $^6A_1(^6S)$ to $^4T_2(^4D)$ and [$^4A_1(^4G)$, $^4E(^4G)$], respectively. The 406 nm excitation band is overlapped with the 414 nm emission band of Eu^{2+}, indicating the possibility of energy transfer from Eu^{2+} to Mn^{2+} in α-$Ca_2P_2O_7$ host [4]. Another evidence for energy transfer in $Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} is that the PLE spectra monitoring the orange emission of the Mn^{2+} and the blue emission of Eu^{2+} are similar.

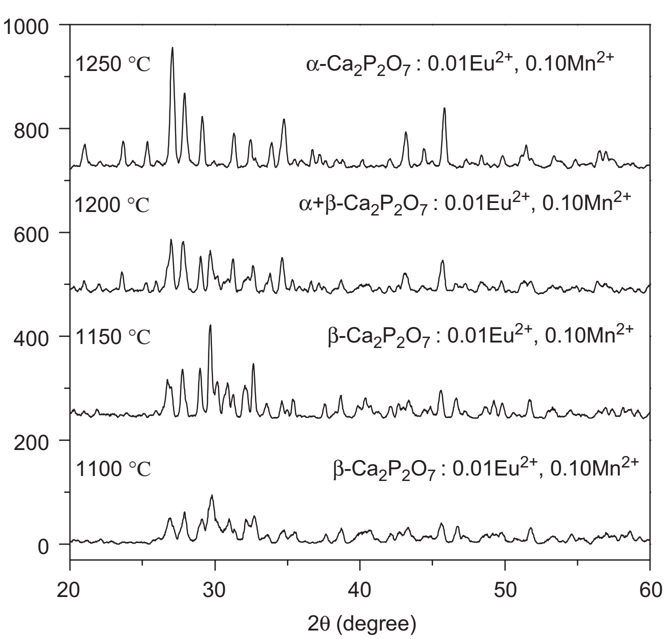

Fig. 1. XRD patterns of $Ca_2P_2O_7$: 0.01Eu^{2+}, 0.10Mn^{2+} sintered at different temperatures.

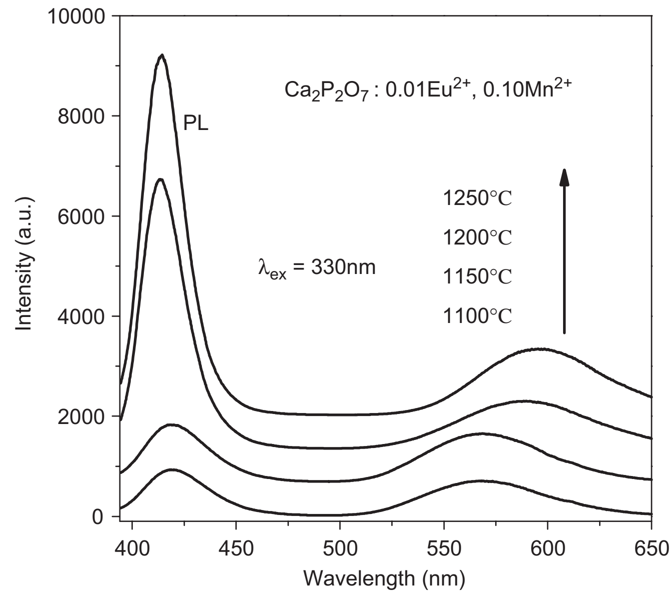

Fig. 2. PL spectra of $Ca_2P_2O_7$: 0.01Eu^{2+}, 0.10Mn^{2+} sintered at different temperatures.

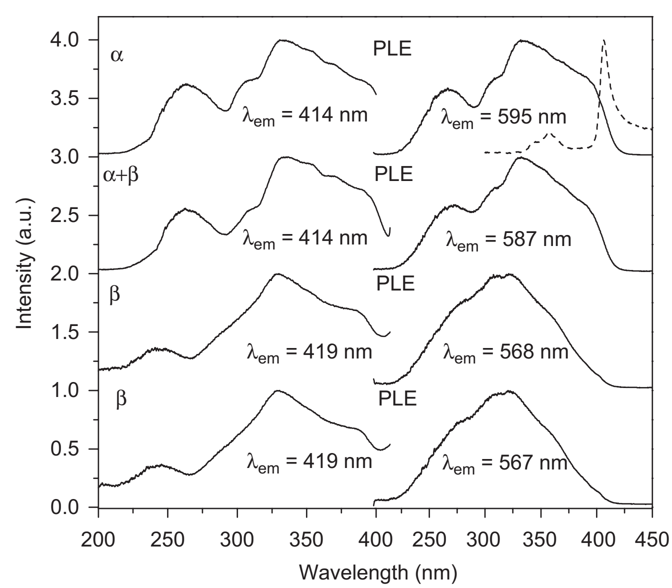

Fig. 3. PLE spectra of $Ca_2P_2O_7$: 0.01Eu^{2+}, 0.10Mn^{2+} sintered at different temperatures and the PLE spectra of $Ca_2P_2O_7$: 0.10Mn^{2+}.

Fig. 4 shows the emission spectra of α- and β-$Ca_2P_2O_7$: 0.01Eu^{2+}, xMn^{2+} ($x = 0.04$, 0.06, 0.08, 0.10, and 0.12), respectively. The remarkable enhancements of the orange band relative to blue band in both phases are observed as increasing Mn^{2+} concentrations. The fluorescence lifetimes of Eu^{2+} in the presence (τ) and absence of Mn^{2+} (τ_0) co-doping are measured and depicted in Fig. 5. The lifetimes are continuously shortened with increasing Mn^{2+} concentrations in both phases, demonstrating the

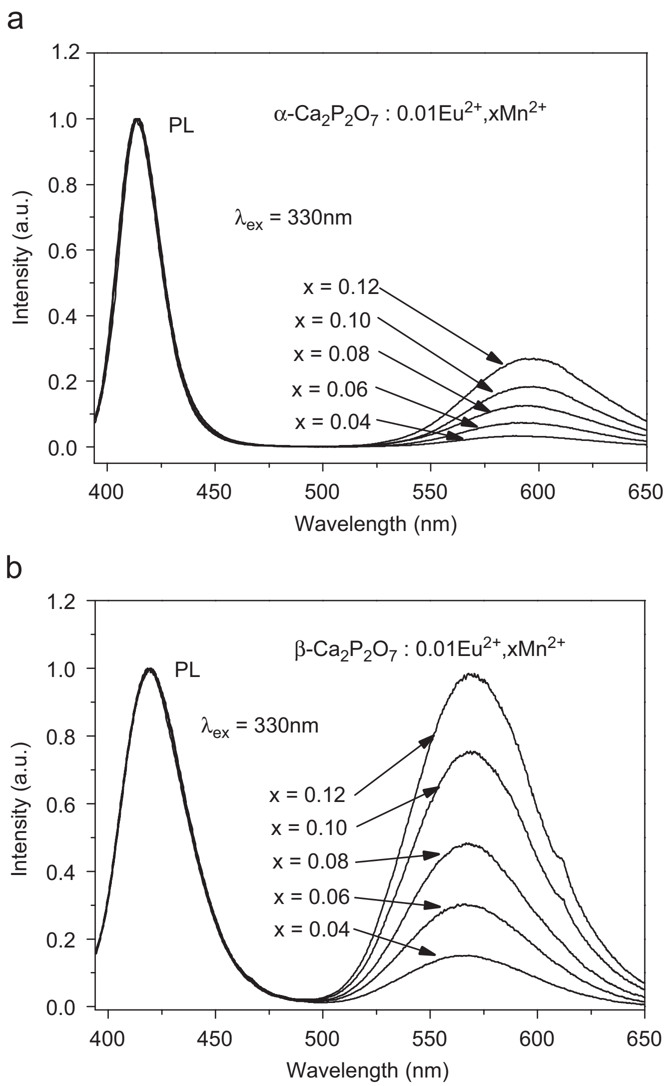

Fig. 4. PL spectra ($\lambda_{ex} = 330$ nm) of α- and β-$Ca_2P_2O_7$: $0.01Eu^{2+}$, xMn^2.

energy transfer from Eu^{2+} to Mn^{2+}[7]. The energy transfer efficiencies (η_T) are calculated using the following equation,

$$\eta_T = 1 - \frac{\tau}{\tau_0}. \quad (1)$$

The results are also depicted in Fig. 5. It can be seen that η_T increase gradually with increasing Mn^{2+} concentrations and the efficiencies in α-$Ca_2P_2O_7$ are higher than that in β-$Ca_2P_2O_7$ for the same doping concentration of Mn^{2+}. However, it is observed that the ratio of orange to blue band in α-$Ca_2P_2O_7$ is lower than that in β-$Ca_2P_2O_7$ for the same doping concentration of Mn^{2+}, as illustrated in Fig. 4. This seemingly incompatible result can be understood by the analysis of the luminescence dynamical process of Eu^{2+} and Mn^{2+} under steady excitation in this host. Considering that the luminescence efficiency of Mn^{2+} is quite high based on the experimental observation that the lifetimes of Mn^{2+} in both phases are nearly unchanged with increasing Mn^{2+} concentrations, the ratio of orange to blue band

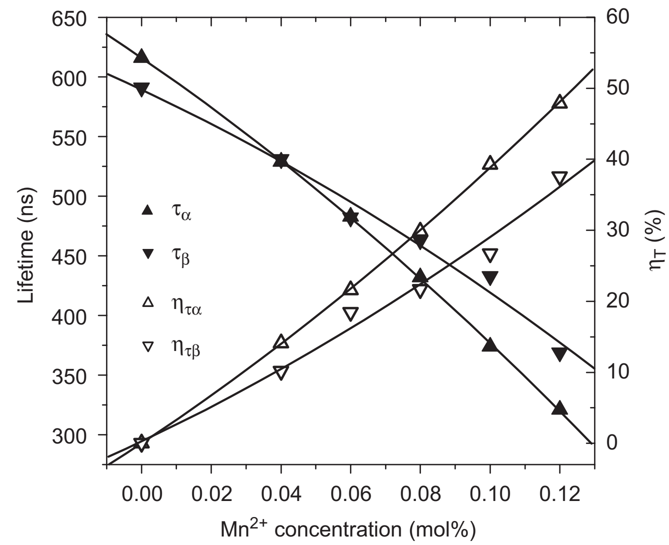

Fig. 5. Lifetime and energy transfer efficiency of α- and β-$Ca_2P_2O_7$: $0.01Eu^{2+}$, xMn^{2+}.

(S_O/S_B) can be expressed as the following equation:

$$\frac{S_O}{S_B} = \frac{\eta_T}{\eta_{Eu}}, \quad (2)$$

where η_{Eu} is the luminescence efficiency of Eu^{2+}.

In Fig. 2, the emission intensity of Eu^{2+} in β-$Ca_2P_2O_7$ is much weaker than that in α-$Ca_2P_2O_7$ for the same doping concentrations. The weak PL intensity of β-phase is not attributed to low converting from Eu^{3+} into Eu^{2+} in sample preparation because there presents a very weak emission traces of Eu^{3+} at 611 nm due to the transition of $^5D_0$–$^7F_2$, as shown in Fig. 4(b) It is thus considered that the luminescence efficiency of Eu^{2+} in β-$Ca_2P_2O_7$ is much lower than that in α-$Ca_2P_2O_7$. Considering that the energy transfer efficiencies in α-$Ca_2P_2O_7$ is just a little higher than that in β-$Ca_2P_2O_7$ for the same concentration of Eu^{2+} and Mn^{2+}, the higher intensity ratio of orange to blue band in β-$Ca_2P_2O_7$ but lower energy transfer efficiencies is mainly due to its lower luminescence efficiency.

4. Conclusions

The phase dependent photoluminescence and energy transfer in $Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} are investigated. Strong orange emission of Mn^{2+} located at 595 nm in α-phase and 568 nm in β-phase $Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} are observed upon UV excitation through energy transfer from Eu^{2+} to Mn^{2+}. The energy transfer efficiencies in α-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} are higher than that in β-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} for the same doping concentration. The PLE spectra of α-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} can cover 400 nm, indicating that α-$Ca_2P_2O_7$: Eu^{2+}, Mn^{2+} can be a promising phosphor with intense orange component for near-UV LED chips-based white LEDs.

Acknowledgement

This work is financially supported by the MOST of China(2006CB601104,2006AA03A138), and by the Natural Science Foundation of China(10574128,10504031).

References

[1] T. Mukai, M. Yamada, S. Nakamura, SPIE 2 (1999) 3621.
[2] J.S. Kim, P.E. Jeon, J.C. Choi, H.L. Park, S.I. Mho, G.C. Kim, Appl. Phys. Lett. 84 (2004) 2931.
[3] W.M. Yen, M.J. Weber, Inorganic Phosphor, New York, CRC, 2004 P. 94, Section 4.
[4] Z.D. Hao, J.H. Zhang, X. Zhang, X.Y. Sun, Y.S. Luo, S.Z. Lu, Appl. Phys. Lett. 90 (2007) 261113.
[5] N.C. Webb, Acta Crystallogr 21 (1966) 942.
[6] C. Calvo, Inorg. Chem. 7 (1968) 1345.
[7] M.M. Broer, D.L. Huber, W.M. Yen, W.K. Zwicker, Phys. Rev. Lett. 49 (1982) 394.