Article ID: 1000-7032(2013)01-0040-05

Full Emission from Single Near-UV Excited Phosphor

XIONG Li, LI Xiao-fan, WANG Zheng-liang*

(The Engineering Laboratory of Polylactic Acid-Based Functional Materials of Yunnan Province, School of Chemistry and Biotechnology, Yunnan University of Nationalities, Kunming 650500, China)

** Corresponding Author, E-mail: wzhl_ww@yahoo.com.cn*

Abstract: A series of samples $2MgO \cdot Al_2O_3 \cdot P_2O_5$ doped with Eu, Tb, Mn were prepared by the solid state reaction at high temperature. And their photo-luminescent properties were investigated. The phosphor $2MgO_{0.95} \cdot Al_2O_3 \cdot P_2O_5$:0.02Eu, 0.02Tb, 0.01Mn can exhibit intense red, green, and blue light emiss under near-UV light excitation. The luminescent properties were investigated and its CIE chromaticity coordinates (0.35, 0.25) are close to white light region. The phosphor has potential application for near-UV emitting diodes.

Key words: phosphors; optical properties; white light

CLC number: O482.31; O614.33 **Document code**: A **DOI**: 10.3788/fgxb20133401.0040

近紫外光激发的单一全发射荧光粉的发光性能

熊 丽, 李小凡, 汪正良*

(云南民族大学化学与生物技术学院 云南省聚乳酸基功能材料工程实验室, 云南 昆明 650500)

摘要: 利用传统的高温固相法合成了 $2MgO \cdot Al_2O_3 \cdot P_2O_5$ 掺 Eu, Tb^{3+}, Mn^{2+} 系列荧光粉,并研究了它们的发光性能。荧光粉 $2MgO_{0.95} \cdot Al_2O_3 \cdot P_2O_5$:0.02Eu, 0.02Tb, 0.01Mn 在近紫外光区具有很强的吸收。在近紫外光激发下,样品发射谱中包含明显的红光、绿光、蓝光3种发射。其CIE色度坐标(0.35, 0.25)接近白光区域,在近紫外发光二极管方面有潜在的应用前景。

关 键 词: 荧光粉; 发光性能; 白光

1 Introduction

Semiconductor-based light-emitting diodes (LEDs) have many advantages, such as high efficiency, long lifetime, low power consumption and environment-friendly characteristics[1-2]. In particular, white light generated by LED is considered to have great potential as solid state light source. The white LED can be generated by several different methods[3-6]. At present, the commonly used method is to mix the red/green/blue tricolor phosphors with a GaN/InGaN chip. This type of white LED can offer superior color uniformity with high color rendering index and excellent light quality. But it also shows some shortcomings, such as, low luminous efficiency and high manufacturing cost[7]. The white

收稿日期: 2012-10-13; **修订日期**: 2012-11-16
基金项目: 国家青年科学基金(21001092); 云南省教育厅科学研究基金(2010Y424); 云南省高校科技创新团队(2010UY08, 2011UY09); 云南省创新团队(2011HC008)资助项目
作者简介: 熊丽(1987-), 女, 湖北荆门人, 主要从事无机发光材料发光性能的研究。
E-mail: 272299028@qq.com, Tel: (0871)5910017

LED based on single phosphor with tri-color emiss has no re-absorption of the blue light by green and red phosphors, compared with the white LED based on the red, green, blue phosphors. In addition, there is no need to mix two or three phosphors during the packaging of LED. Hence the luminous efficiency and color rendering index can be enhanced. In order to improve the luminous efficiency and reduce the fabricating cost of white LEDs, single phase phosphors with full-color emiss are preferred. Herein, new phosphors $2MgO \cdot Al_2O_3 \cdot P_2O_5$ doped with Eu, Tb^{3+}, Mn^{2+} were investigated, and they show intense red, green and blue emiss under near-UV light excitation.

2 Experiments

The samples $2MgO \cdot Al_2O_3 \cdot P_2O_5$ doped with Eu, Tb^{3+}, Mn^{2+} were prepared with solid-state reaction technique at high temperature. The stoichiometric mixtures of MgO (A. R.), $Al(OH)_3$ (A. R.), $NH_4H_2PO_4$ (A. R.), $MnCO_3$ (A. R.), Eu_2O_3 (99.99%) and Tb_4O_7 (99.99%) were heated at 1 400 ℃ in CO atmosphere for 4 h. The structure of the final products was determined by X-ray powder diffraction (XRD) using Cu Kα radiation on RIGAKU D/max 2200 vpc X-ray diffractometer. The excitation and emission spectra were recorded on a JOBIN YVON FL3-21 spectrofluorometer at room temperature and a 450 W xenon lamp was used as excitation source.

3 Results and Discussion

It is well known that the excitation and emission of Eu^{2+} are broad band in many hosts, which is beneficial to the application on phosphor-conversion light-emitting diodes[8-9]. Such as Sr_2SiO_4 doped with Eu^{2+} was used as yellow phosphor for GaN chip[8], and $Sr_3MgSi_2O_8$ doped with Eu^{2+} was used for near UV InGaN chip[9]. Here we first investigated the photoluminescent properties of Eu doped $2MgO \cdot Al_2O_3 \cdot P_2O_5$. The excitation and emission spectra of $2MgO \cdot Al_2O_3 \cdot P_2O_5:0.02Eu$ are shown in Fig. 1. The broad excitation band from 250 nm to 410 nm in curve (a) of Fig. 1 is due to 4f-5d transit of Eu^{2+} in the host lattices. The excitation band at ~260 nm of curve (b) is attributable to charge transfer (CT) transition of the host, and the sharp lines in 300 ~ 550 nm range are intra-configurational 4f-4f transit of Eu^{3+} in the host lattices. For the $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transit at ~395 and ~465 nm, there are also two strong absorpt. This result shows that both Eu^{2+} and Eu^{3+} co-exist in this phosphor. Curves (c) and (d) in Fig. 1 are the emission spectra under excitation of 300 and 395 nm, respectively. In fact blue and red light emission can be observed in these two curves. The broad blue emission at ~ 435 nm is due to the electronic transition between $4f^7$ ground and $4f^65d^1$ excited state of Eu^{2+}. The mainly red emission is due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 613 nm, other transit, such as $^5D_0 \rightarrow {}^7F_J$ transit in 570 ~ 720 nm range and $^5D_1 \rightarrow {}^7F_J$ transit in 520 ~ 570 nm range, are very weak. Comparing curves (c) and (d), the intensity ratio of blue to red emission is different. The ratio of blue light to red light emission under 300 nm excitation is obviously higher than that under 395 nm excitation. The result is in good agreement with the excitation spectra.

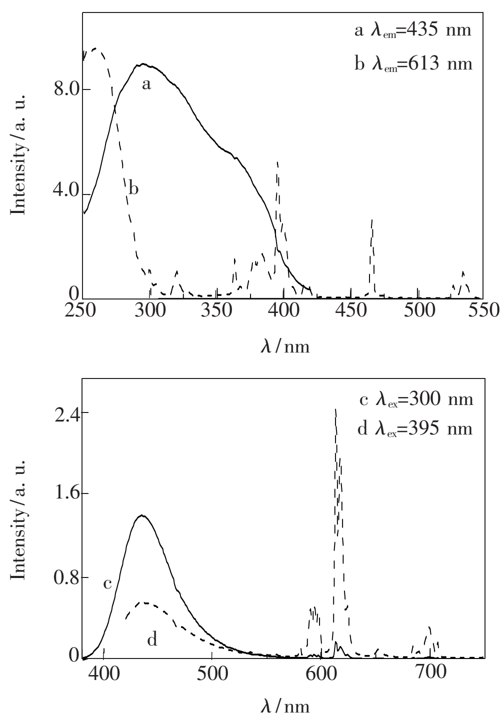

Fig. 1 The excitation and emission spectra of the phosphor $2MgO \cdot Al_2O_3 \cdot P_2O_5:0.02Eu$

The Tb^{3+} can produce intense green light emission in many hosts[10-13]. As discussed above, the blue and red light emission can be observed in the phosphor $2MgO \cdot Al_2O_3 \cdot P_2O_5$:0.02Eu simultaneously. Then the red, green and blue light emiss are expected from the phosphor $2MgO \cdot Al_2O_3 \cdot P_2O_5$: Eu doped with Tb^{3+}. Mn^{2+} is also a very good sensitizer of red luminescence in many hosts[7,14-15] and the red emission of Mn^{2+} is a broad band, which can enhance the color reproducibility of the white light. So the phosphors $2MgO_{0.98-x-y} \cdot Al_2O_3 \cdot P_2O_5$: 0.02Eu, xTb, yMn were prepared and their luminescent properties were investigated as follows. The excitation spectra of the phosphors $2MgO_{0.98-x-y} \cdot Al_2O_3 \cdot P_2O_5$: 0.02Eu, xTb, yMn (x = 0.01, 0.02. y = 0.005, 0.01) monitored at 435 nm are shown in Fig. 2(a). These four curves are of the similar shapes, but the excitation intensity is different. With the increasing of Tb^{3+} and Mn^{2+} content, the intensity of the excitation is decreasing, this means the introduction of the Tb^{3+} and Mn^{2+} decrease the blue emission. Fig. 2(b) is the excitation spectra of the phosphors $2MgO_{0.98-x-y} \cdot Al_2O_3 \cdot P_2O_5$: 0.02Eu, xTb, yMn(x = 0.01, 0.02. y = 0.005, 0.01) monitored at 544 nm. The excitation peaks of the 4f-4f transit of Tb^{3+} in many hosts appear in the range 360 ~ 550 nm. Comparing with Fig. 2(a), a few sharp peaks (such as the peak at ~ 370 nm) can be observed in Fig. 2(b), and some peaks are overlapped by the excitation band of Eu^{2+}. These sharp peaks are assigned to the intra-configurational 4f-4f transit of Tb^{3+} in the host. The excitation intensity increased with the improvement of Tb^{3+} content. In the host of Fig. 2(c), only the $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+} can be observed, and other 4f-4f transit are overlapped. The excitation from 300 nm to 400 nm is a broad band. This is useful to absorb the near UV light emitted by the near UV LED chips. The excitation intensity increased with Mn^{2+} content, but decreased with Tb^{3+} content. This result shows the introduction of Mn^{2+} is useful to enhance the red emission. However, the Tb^{3+} will decrease the red emission.

Fig. 3 shows the emission spectra of the phosphor

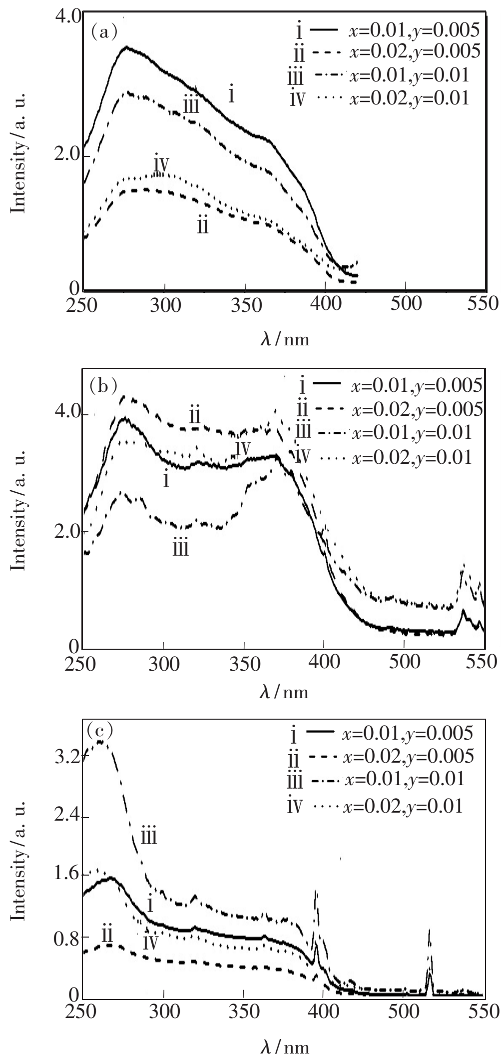

Fig. 2　The excitation spectra of the phosphor $2MgO_{0.98-x-y} \cdot Al_2O_3 \cdot P_2O_5$: 0.02Eu, xTb, yMn. (a) λ_{em} = 435 nm. (b) λ_{em} = 544 nm. (c) λ_{em} = 613 nm.

$2MgO_{0.98-x-y} \cdot Al_2O_3 \cdot P_2O_5$: 0.02Eu, xTb, yMn under 395 and 370 nm excitation, respectively. As shown in Fig. 3(a), the red, green, and blue emission can be observed. The blue emission at ~ 440 nm is the $4f^7$-$4f^65d^1$ transit of Eu^{2+}. And the green emission at ~ 544 nm is mainly due to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}, other $^5D_4 \rightarrow {}^7F_J$ transit are very weaker. The strongest red emission is at ~ 613 nm, which is due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. A broad emission from 560 nm to 720 nm can be observed, which is overlapped by the red emission of Eu^{3+}. This broad emission is ascribed to the $^4T_1 \rightarrow {}^6A_1$ transit of $^3d_5$ levels of Mn^{2+}. Fig. 3(b) is the emission spectra under 370 nm excitation. As same as the Fig. 3(a), three kinds color emiss can

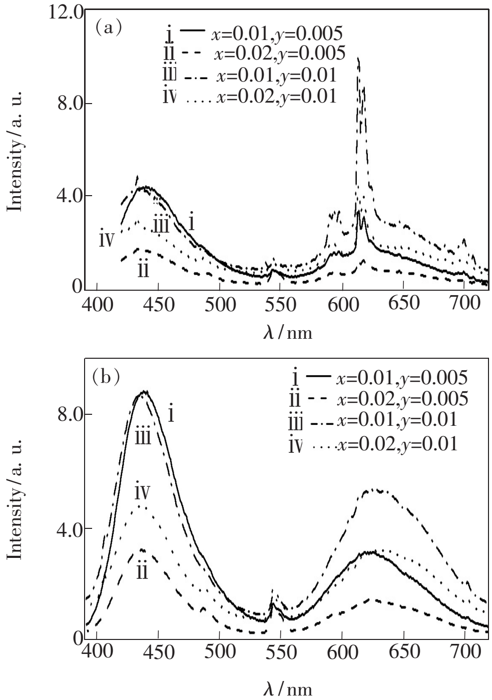

Fig. 3　The emission spectra of the phosphor $2MgO_{0.98-x-y}$ · Al_2O_3 · P_2O_5: 0.02Eu, *x*Tb, *y*Mn. (a) λ_{ex} = 395 nm. (b) λ_{ex} = 370 nm.

be observed also. However, the red emission in Fig. 3(b) is mainly due to the ${}^4T_1 \rightarrow {}^6A_1$ transit of $3d^5$ levels of Mn^{2+}, and the red emission of Eu^{3+} at ~ 613 nm is overlapped by the emission of Mn^{2+}.

The CIE chromaticity coordinates for the emission of the phosphors 2MgO · Al_2O_3 · P_2O_5: 0.02Eu, *x*Tb, *y*Mn under 395 nm excitation are calculated, and they were shown in Fig. 4. With the increased Tb^{3+} and Mn^{2+} content, the CIE chromaticity coordinates of the phosphor is close to the white light region. The CIE chromaticity coordinates of $2MgO_{0.95}$ · Al_2O_3 ·

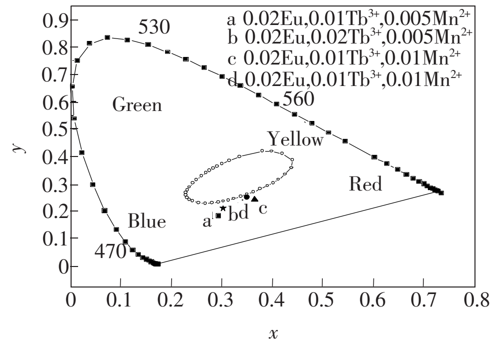

Fig. 4　The CIE chromaticity coordinates (*x*, *y*) of the phosphors $2MgO_{0.98-x-y}$ · Al_2O_3 · P_2O_5: 0.02Eu, *x*Tb, *y*Mn under 395 nm excitation in the CIE 1931 chromaticity diagram.

P_2O_5: 0.02Eu, 0.02Tb, 0.01Mn are calculated to be $x = 0.35$, $y = 0.2$ (Fig. 4d).

4　Conclusion

In conclusion, new phosphors 2MgO · Al_2O_3 · P_2O_5: Eu, Tb, Mn with full color emiss were prepared by the solid state reaction, and their photoluminescent properties were investigated. The blue emission originates from the Eu^{2+}, and the green emission is mainly due to the ${}^5D_4 \rightarrow {}^7F_5$ transit of Tb^{3+} in the host. The red light is ascribed to the 4f-4f transit of Eu^{3+} and the ${}^4T_1 \rightarrow {}^6A_1$ transit of Mn^{2+}. The phosphor $2MgO_{0.95}$ · Al_2O_3 · P_2O_5: 0.02Eu, 0.02Tb, 0.01Mn shows intense tri-color emiss under 395 nm light excitation, and its CIE chromaticity coordinates ($x = 0.35$, $y = 0.25$) are close to the white light region. It may be a potentially full-color phosphor for near UV white LEDs.

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