

# Luminescence Properties of Eu/Tb Activated $Y_2O_3$ Phosphors Synthesized by Solid State Process

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**Abstract:** Rare-earth doped phosphors with tunable optical properties have potential applications in solid state lighting, such as display panels and fluorescent lamps. Herein, trivalent  $Eu^{3+}$ ,  $Tb^{3+}$  activated  $Y_2O_3$  phosphors were synthesized by a solid state process. The phase structure was analyzed by X-ray diffraction. The results show the pure phase of  $Y_2O_3$  is obtained and RE ions do not exhibit any effect on the structural properties. Single RE ions activated  $Y_2O_3$  phosphors display their characteristic emission. With  $Tb^{3+}$  doped in  $Y_2O_3$ , a bright green emission is obtained; when  $Eu^{3+}$  is introduced into the material  $Y_2O_3:Tb^{3+}$ , the emission color can be adjusted to white light. The calculated CIE chromaticity coordinates of RE ions activated  $Y_2O_3$  phosphors confirm the green and white emissions.

**Key words:** rare earth;  $Y_2O_3$ ;  $Eu^{3+}$ ,  $Tb^{3+}$ ; luminescence; phosphor

White light-emitting diodes (LEDs) as the so-called fourth generation solid-state light have attracted considerable attention in recent years because of their extensive applications in display areas based on their excellent characteristics, such as small volume, long lifetime, high energy efficiency, energy-saving, and environment friendly<sup>[1-5]</sup>. Generally, the tri-band white LEDs are fabricated by pumping the UV-A (320~400 nm) LED sources. However, nowadays, deep UV LEDs with the emission wavelengths in the UV-B (280~315 nm) and UV-C (180~280 nm) regions of the electromagnetic spectrum have been developed to fabricate the tri-band based white LEDs<sup>[6-8]</sup>. These UV-B or UV-C based white LEDs are potentially used for medical applications<sup>[9-11]</sup>. Hence, the availability of high-quality phosphors operating under UV excitation is a key factor for better performance of such LEDs. In the case of the tri-band white LED, inorganic oxides would be good candidates for RGB phosphors in terms of both chemical stability and luminescence efficiency.

Yttrium oxide ( $Y_2O_3$ ) has been investigated as a good host lattice for trivalent rare earth cations<sup>[12, 13]</sup>. Rare earths (RE) doped yttrium phosphors has applications in cathode radiation tube, field emission display and thin film electroluminescence

devices due to their excellent chemical stability, low volatility in vacuum and absence of corrosive gas emission under electron bombardment<sup>[14-17]</sup>. In the present paper, we reported the structure and color tunable luminescence properties of trivalent rare-earth (RE) ions  $Tb^{3+}/Eu^{3+}$  activated  $Y_2O_3$  powders using a solid state method. The structures were studied by X-ray diffraction (XRD) patterns.  $Eu^{3+}$ ,  $Tb^{3+}$  singly activated  $Y_2O_3$  phosphors showed their characteristic emission. The  $Eu^{3+}$ ,  $Tb^{3+}$  ions co-activated  $Y_2O_3$  phosphor exhibited white light emission by controlling the concentrations. The details of photoluminescence (PL) properties were also discussed.

## 1 Experiment

Powder samples were synthesized by a solid-state reaction method.  $Y_2O_3$  (99.9%),  $Eu_2O_3$  (99.99%), and  $Tb_4O_7$  (99.99%) were used as starting materials. Firstly, the stoichiometric amount of raw materials  $Y_2O_3$ ,  $Eu_2O_3$  and  $Tb_4O_7$  were weighed, and then were thoroughly ground in an agate mortar. Afterwards, the mixtures were placed in crucibles. Next, they were sintered at 1000 °C for 6 h in a box-type furnace and cooled down to room temperature naturally.

Received date: November 14, 2015

Foundation item: National Nature Science Foundation of China (11104366); Natural Science Foundation Project of Chongqing (cstc2014jcyjA50018)

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Phase purity was examined by XRD using a maxima-X 7000 powder diffractometer. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded at room temperature using a Hitachi F-4600 fluorescence spectrometer with a 150-W xenon lamp as the excitation source. The emission spectra of all samples were measured at a fixed band-pass of 0.2 nm with the same instrument parameters.

## 2 Results and Discussion

XRD patterns of  $\text{Y}_2\text{O}_3:2\%\text{Eu}^{3+}$ ,  $\text{Y}_2\text{O}_3:2\%\text{Tb}^{3+}$  and  $\text{Y}_2\text{O}_3:2\%\text{Eu}^{3+}, 2\%\text{Tb}^{3+}$  are shown in Fig.1. They are the XRD patterns of  $\text{Y}_2\text{O}_3$ , which are consistent with JCPDS 88-1040 ( $\text{Y}_2\text{O}_3$ , space group  $\text{Ia}\bar{3}$ ). No other phase can be detected, indicating that the  $\text{RE}^{3+}$  ions are completely dissolved in the  $\text{Y}_2\text{O}_3$  host and the rare earth ions doping does not change the lattice of  $\text{Y}_2\text{O}_3$ .

Fig.2 shows the PL excitation and emission spectra of  $\text{Y}_2\text{O}_3:2\%\text{Eu}^{3+}$  phosphors. The excitation spectrum of  $\text{Y}_2\text{O}_3:2\%\text{Eu}^{3+}$  monitoring the emission at 613 nm of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions can be divided into two parts: one part is from 230 nm to 300 nm with a charge transfer band (CTB) of  $\text{O}^{2-}-\text{Eu}^{3+}$ , and the other maximum at 228 nm which is attributed to the part from 300 nm to 500 nm consists of f-f transitions of  $\text{Eu}^{3+}$  ions. Under 254 nm excitation, bright red luminescence appears to the naked eye, as shown in the insert figure. There is a major red emission peak at 613 nm corresponding to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions with some other weak peaks assigned to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  in the range from 500 nm to 750 nm<sup>[18]</sup>, as assigned in Fig.2.

Fig.3 presents the PL and PLE spectra of the  $\text{Y}_2\text{O}_3:2\%\text{Tb}^{3+}$  sample. The excitation spectrum, monitoring the emission at 544 nm of the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transitions, consists of several broad bands with peaks at 212, 227, 271 and 299 nm, which correspond to the  $4f^8 \rightarrow 4f^75d$  transition allowed by the electric dipolar parity<sup>[19]</sup>. These broad excitation bands cannot be assigned to  $\text{Tb}^{3+}-\text{O}^{2-}$  charge-transfer (CT) transition because the CT states have much higher energy than 5d states of  $\text{Tb}^{3+}$ <sup>[20]</sup>. Under 210 nm excitation, the emission spectrum of  $\text{Y}_2\text{O}_3:2\%$

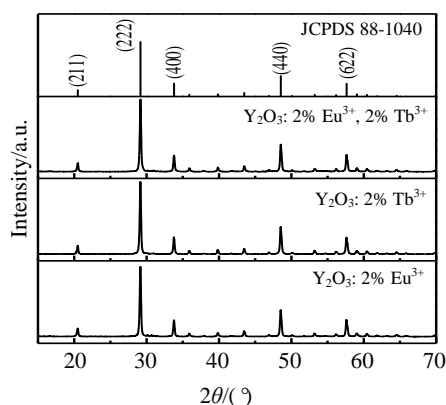


Fig.1 XRD patterns of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ ,  $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ , and  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Tb}^{3+}$  phosphors (JCPDS card No. 88-1040)

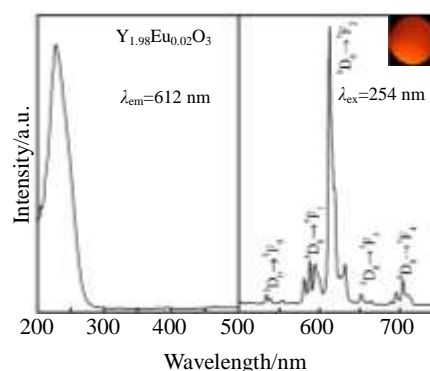


Fig.2 Excitation spectrum of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphors and emission spectrum of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphors

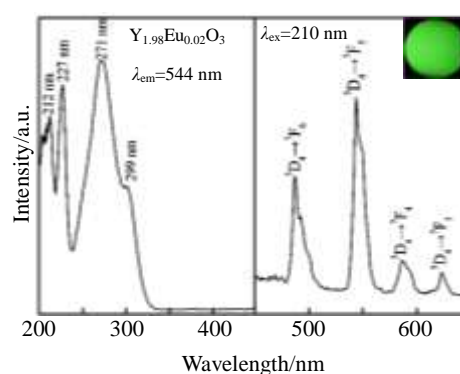


Fig.3 Excitation spectrum of  $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$  phosphors and emission spectrum of  $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$  phosphors

$\text{Tb}^{3+}$  yields green emissions from 480–650 nm, due to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$  ( $J = 3, 4, 5, 6$ ) transitions. Specifically, the emission at 488, 544, 587 and 624 nm are attributed to the transitions of  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ ,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ ,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$  and  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$ , respectively. The dominated green emission at 544 nm is corresponding to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition of  $\text{Tb}^{3+}$ .

Fig.4 shows the emission spectrum of the codoped  $\text{Y}_2\text{O}_3:2\%\text{Tb}, 0.2\%\text{Eu}$  under 210 nm excitation. While the concentrations of Tb and Eu are 2% and 0.2%, white light-emitting phosphor is obtained. The white emission as shown in the insert is obtained by blending the  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  in  $\text{Y}_2\text{O}_3$ .

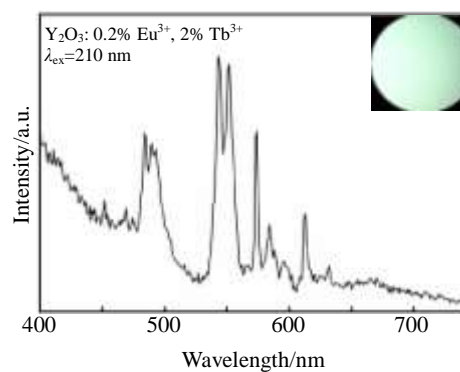


Fig.4 Emission spectrum of  $\text{Y}_{1.978}\text{Eu}_{0.002}\text{Tb}_{0.02}\text{O}_3$  phosphors

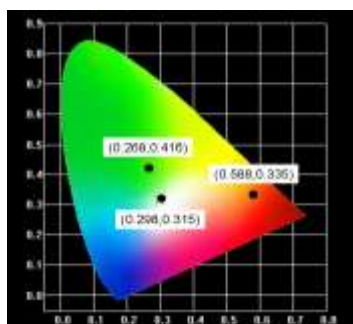


Fig.5 CIE chromaticity diagram of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  (0.588, 0.335),  $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$  (0.268, 0.416) and  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}/\text{Tb}^{3+}$  (0.298, 0.315) phosphors

Fig.5 shows the Commission International de l'Eclairage (CIE) chromaticity coordinates of  $\text{Y}_2\text{O}_3:\text{Tb}$ ,  $\text{Y}_2\text{O}_3:\text{Eu}$  and  $\text{Y}_2\text{O}_3:\text{Tb}/\text{Eu}$  phosphors. The (x,y) coordinates vary from red (0.588, 0.335), green (0.268, 0.416) and white (0.298, 0.315). It indicates that  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  are truly the single-phased white phosphors.

### 3 Conclusions

1) Rare earth  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions doped  $\text{Y}_2\text{O}_3$  phosphors are synthesized by solid state process. The pure phase  $\text{Y}_2\text{O}_3$  is only found in the phosphors. RE ions do not have any effect on the structural properties.

2) The single RE ion doped  $\text{Y}_2\text{O}_3$  phosphor exhibits good luminescence properties in their respective areas. The photoluminescent examination reveal bright green phosphorescence for  $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$ . When these phosphors are codoped with  $\text{Eu}^{3+}$ , their emission color can be controlled from bright green to bright red. And white light phosphor can be obtained while the concentration of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  is 0.2% and 2%, respectively.

3) This fine adjusting along with the scalable process for synthesis of these phosphors may facilitate their employment in several applications.

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## Eu/Tb 共掺杂 $\text{Y}_2\text{O}_3$ 荧光粉的发光性质研究

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**摘要:** 稀土掺杂荧光粉在固态照明中有良好的应用前景。这里用固相法合成了  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}, \text{Tb}^{3+}$  荧光粉, 粉的相结构用 X 射线衍射仪进行了表征, 发现合成了纯相  $\text{Y}_2\text{O}_3$ , 掺杂的稀土离子未对基质结构产生影响。稀土离子单掺杂的  $\text{Y}_2\text{O}_3$  荧光粉在各自特征领域表现出良好的发光性质,  $\text{Y}_2\text{O}_3:\text{Tb}^{3+}$  发射出亮绿光, 而  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  发射出亮红光颜色。调控它们的浓度, 可以在  $\text{Y}_2\text{O}_3:0.2\% \text{Eu}^{3+}, 2\% \text{Tb}^{3+}$  处实现白光, 详细分析了它们的发光光谱, 计算了它们的色坐标, 对应的 CIE 色坐标分别标记在色坐标图中。

**关键词:**  $\text{Y}_2\text{O}_3:\text{Eu}, \text{Tb}$ ; 荧光粉; 发光性质