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

Jin Ye^{1,2}, Zhou Hongpeng², Zhang Dingfei¹

¹ Chongqing University, Chongqing 400044, China; ² Chongqing University of Technology, Chongqing 400054, China

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^[1-5]. Generally, the triband 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^[6-8]. These UV-B or UV-C based white LEDs are potentially used for medical applications^[9-11]. 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^[12, 13]. 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^[14-17]. 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.

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Corresponding author: Jin Ye, Ph. D., Associate Professor, School of Science, Chongqing University of Technology, Chongqing 400054, P. R. China, Tel: 0086-23-62563051, E-mail: jinye@cqut.edu.cn

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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 Y_2O_3 , which are consistent with JCPDS 88-1040 (Y_2O_3 , space group $\text{Ia}\bar{3}$). No other phase can be detected, indicating that the RE^{3+} ions are completely dissolved in the Y_2O_3 host and the rare earth ions doping does not change the lattice of Y_2O_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 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 redemission 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^[18], 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 $4\text{f}^8 \rightarrow 4\text{f}^75\text{d}$ transition allowed by the electric dipolar parity^[19]. 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 Tb^{3+} ^[20]. 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

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 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 Tb^{3+} and Eu^{3+} in Y_2O_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 $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Tb^{3+} are truly the single-phased white phosphors.

3 Conclusions

1) Rare earth Tb^{3+} and Eu^{3+} ions doped Y_2O_3 phosphors are synthesized by solid state process. The pure phase Y_2O_3 is only found in the phosphors. RE ions do not have any effect on the structural properties.

2) The single RE ion doped Y_2O_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 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 Eu^{3+} and 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 Y_2O_3 荧光粉的发光性质研究

金 叶^{1,2}, 周虹鹏², 张丁非¹

(1. 重庆大学, 重庆 400044)

(2. 重庆理工大学, 重庆 400054)

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 Y_2O_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 Y_2O_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

作者简介: 金 叶, 女, 1982 年生, 博士, 副教授, 重庆理工大学理学院, 重庆 400054, 电话: 023-62563051, E-mail: jinye@cqut.edu.cn