

A potential red-emitting phosphor $\text{In}_2(\text{WO}_4)_3:\text{Eu}^{3+}$ for white LEDs and its luminescence properties

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$\text{In}_{2-x}(\text{WO}_4)_3:\text{xEu}^{3+}$ red phosphors were synthesized by a high temperature solid-state reaction in air. X-ray diffraction (XRD), laser particle size analyzer and molecular fluorescence spectrometer were used to respectively investigate the structures, size distribution and luminescence properties. The XRD result displays the as-prepared phosphor with no impurity phase, and doping Eu^{3+} in the $\text{In}_2(\text{WO}_4)_3$ cannot change the host crystal structure. The particle size exhibits a normal size distribution with the average diameter of around 2.4 μm serving the coating of manufacturing LED. The excitation spectrum reveals that the phosphor can be effectively excited under the excitation of near-UV or blue light. In the emission spectrum, the greatest red emission at 611nm resulting from the Eu^{3+} transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ was found. The photoluminescence intensity is dependent on the concentration of Eu^{3+} , and the optimal Eu^{3+} -doped concentration is 15mol%. Considering good luminescence performance of the phosphor, the $\text{In}_2(\text{WO}_4)_3:\text{Eu}^{3+}$ is suggested to be a promising red-emitting material for white LEDs.

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1. Introduction

White light-emitting diodes (LEDs) have been paid much attention to owing to many advantages such as saving energy, long lifetime, high efficiency, and environmental friendliness[1-5]. Being a novel solid-state lighting source, the white LEDs are regarded as the new generation lighting devices in accord with the requirements of green lighting[6-8]. So nowadays the technology of white LEDs has made rapid progress since the first commercial LED for lighting fabricated by Nichia Chemical Company of Japan [9-11]. Several methods are employed to produce white LEDs including phosphor conversion, multiple chips, quantum well and organic white LEDs. Among these methods, the last three with a few drawbacks involving low efficiency and high costs as well as difficulties in production are subject to many application restrictions[12-17]. Compared with these approaches, the emphasis about creating white LEDs has been put on the phosphor-converted method which can meet with the demands of industrial manufacturing[18]. Therefore, this method has aroused main concern and become the one of investigation issues.

At present the white LEDs can be generated by means of phosphor conversion consisting of two primary ways[19-24]. One is a commercially mellow strategy with the combination of the blue InGaN chip and phosphors such as the method by assembling yellow phosphor in

the device of blue LED. The other is a procedure using a UV or near-UV InGaN chip coated tricolor (RGB) phosphors. Both of them, red phosphors play an important role in the regulation of color temperature as well as the improvement of color rendering index (CRI) for white LEDs. Currently commercially red phosphors for white LEDs are based on $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ [25-27]. With the commercial blue phosphor of $\text{ZnS}:(\text{Cu}^+, \text{Al}^{3+})$ and green phosphor of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM), comparison, there are a few defects on the $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ red phosphor[28-33]. For example, this phosphor has low luminescence efficiency and absorbs poor near-UV light. At the same time, the phosphor is chemically unstable so that it can release the H_2S gas when excited by near-UV radiation, which reduces the lifetime of white LEDs. Accordingly, much work has been carried out to exploit high-quality red phosphors used as white LEDs.

Tungstates doped with rare earth ion of Eu^{3+} can be effectively excited by near-UV and blue light to emit red light[34-37]. In addition, the synthesis temperature of tungstates is not high and the phosphor has good stability. Thus this material is attracted by the researchers in order to improve the quality of white LEDs. Lee et al. studied the Eu^{3+} -doped $\text{A}_{4-3x}(\text{WO}_4)_2:\text{Eu}_x^{3+}$ (A=Li, Na, K) and $\text{B}_{(4-3x)/2}(\text{WO}_4)_2:\text{Eu}_x^{3+}$ (B=Mg, Ca, Sr) phosphors and the findings confirmed that these phosphors exhibited a strong absorption in the near UV to green range[38]. Consequently, Long et al. synthesized red-emitting

phosphor $\text{Sr}(\text{La}_{0.75}\text{Eu}_{0.25})_2\text{Mg}_2\text{W}_2\text{O}_{12}$ by solid-state reaction and its emission intensity is approximately three times higher than that of the commercial red phosphor $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ under the blue light[39]. Recently, Zhang et al. prepared stable $\text{CaWO}_4:\text{Eu}^{3+}$ phosphors by the hydrothermal method and the result reveals that the phosphors is a potential red-emitting substitute for blue LED applications[40]. From the prior studies, it can be found that the tungstate may be an ideal host of red phosphor.

On the basis of the above analysis, Eu^{3+} -doped tungstate phosphors were prepared and their photoluminescence properties were also studied in the present paper.

2. Experimental

2.1 Synthesis

The $\text{In}_2(\text{WO}_4)_3:\text{Eu}^{3+}$ samples were synthesized by the conventional solid-state reaction in high temperature. The starting materials were the analytic reagent of tungsten oxide (WO_3), High-purity indium oxide (In_2O_3 , 99.99%) and europium oxide (Eu_2O_3 , 99.99%). All of the raw materials were weighed in stoichiometric proportions. After these materials were thoroughly mixed by the way of grinding in an agate mortar for 20min, the homogeneous mixture was shifted into a corundum crucible and pre-fired at 500°C for 2h in an electric furnace under the air atmosphere. Then it was heated at 1000°C for 6h and the final samples were prepared by cooling down to ambient temperature in the furnace.

2.2 Characterization

The samples were characterized by powder X-ray diffraction (XRD) using a Shimadzu diffractometer with the scanning angle 2θ from 10°C to 70°C under $\text{Cu K}\alpha$ radiation at 40 kV and 150 mA in order to be sure of the crystal structure. The particle size distribution was tested on a Rise-2002 laser particle size analyzer under the dispersant of distilled water. The Photoluminescence spectra were measured employing an RF-5301 molecular fluorescence spectrometer with a Xe lamp as the source of excitation. Both of the excitation and emission slit width were at 3nm. All of the measurements were performed at ambient temperature in the air.

3. Results and discussion

3.1 XRD characterization and size distribution

Fig. 1 is the XRD pattern of the powder $\text{In}_{1.7}(\text{WO}_4)_3:0.3\text{Eu}^{3+}$. All the diffraction peaks of the as-prepared sample are roughly equated with the Joint

Committee on Powder Diffraction Standards (JCPDS) No. 49-0337. It is demonstrated that the dopant ions of Eu^{3+} do not make the host structure change. Additional diffractions which could be attributed to impurities and shift of diffraction peaks that might result from the change of crystal structural parameters are not discovered. According to the PDF#49-0337 card, $\text{In}_2(\text{WO}_4)_3$ has an orthorhombic crystal structure with the unit cell parameters of $a=0.9487\text{nm}$, $b=0.9635\text{nm}$ and $c=1.3349\text{nm}$. Moreover, In^{3+} has the same valencies as the Eu^{3+} , and it could be deemed that In^{3+} ions are substituted by Eu^{3+} ions in the host of $\text{In}_2(\text{WO}_4)_3$.

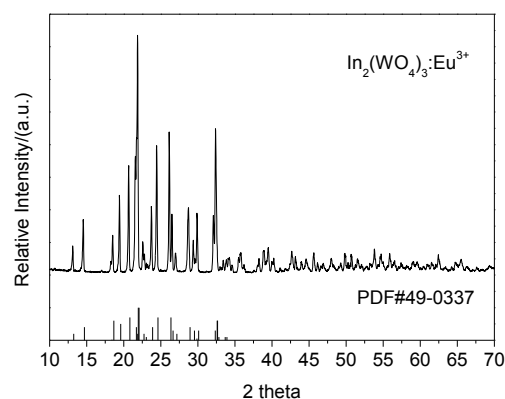


Fig. 1. XRD pattern of the sample $\text{In}_{1.7}(\text{WO}_4)_3:0.3\text{Eu}^{3+}$

The particle size distribution of the powder $\text{In}_{1.7}(\text{WO}_4)_3:0.3\text{Eu}^{3+}$ is illustrated in Fig. 2. The size distribution is close to normal and the average diameter is $2.4\mu\text{m}$ or so, which suits the needs for coating in the manufacture of solid-lighting devices[41].

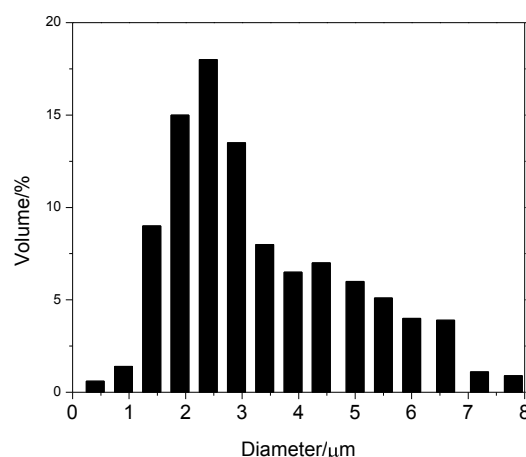


Fig. 2. Particle size distribution of the powder $\text{In}_{1.7}(\text{WO}_4)_3:0.3\text{Eu}^{3+}$

3.2 Analysis on the excitation and emission spectra

The excitation spectrum of the phosphor $\text{In}_{1.85}(\text{WO}_4)_3:0.15\text{Eu}^{3+}$ is recorded by monitoring at 610 nm, as shown in Fig. 3. There are three major excitation peaks located at 393nm, 464nm and 535nm, which are narrow absorbing peaks derived from the f-f transition of Eu^{3+} in accordance with ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, respectively[42]. Besides, the left broad excitation peaks are charge-transfer band. The intensity of Eu^{3+} energy level transition is obviously higher than the charge transfer in the sample while some materials manifest the opposite phenomenon, which is probably related to the energy transfer for electron cloud between the cation and anion in the host. On the whole, from the viewpoint of application for white LEDs, the $\text{In}_2(\text{WO}_4)_3:\text{Eu}^{3+}$ phosphor has the relatively strong absorption of near-UV or blue light, which matches well with the output wavelength of current using LED. The result suggests that the $\text{In}_2(\text{WO}_4)_3:\text{Eu}^{3+}$ might be a potential red-emitting phosphor for white LEDs.

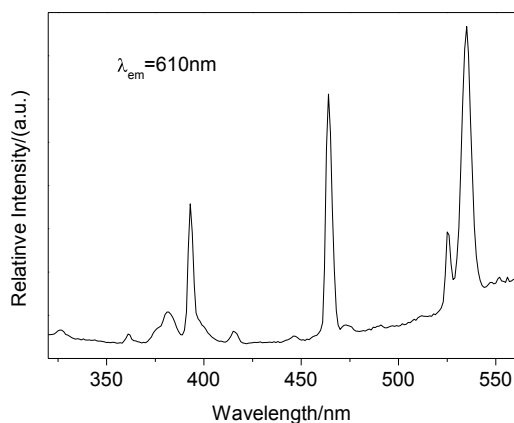


Fig. 3. The excitation spectrum of the phosphor $\text{In}_{1.85}(\text{WO}_4)_3:0.15\text{Eu}^{3+}$ monitored at 610nm.

Fig. 4 shows the emission spectrum of the phosphor $\text{In}_{1.85}(\text{WO}_4)_3:0.15\text{Eu}^{3+}$ excited at 610 nm. The two main emission peaks are observed in the spectrum. One is the red light with the wavelength of 611nm and the other is the reddish orange light of 591 nm. The lights separately spring from the Eu^{3+} transfer of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electric dipole and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ magnetic dipole. The former transition intensity is apparently greater than the latter, which displays the Eu^{3+} occupying the site of inversion center[43]. Thanks to the Eu^{3+} existing the ligand field of orthorhombic crystal lattice and this field acting on the Eu^{3+} ions, the Stark split about the energy level of Eu^{3+} emerges. As a result, the energy level split of ${}^7\text{F}_2$ is revealed in the spectrum.

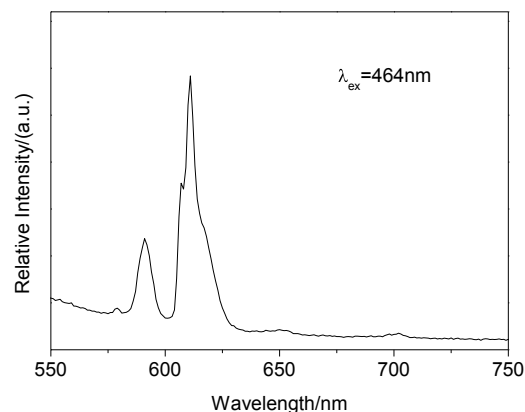


Fig. 4. The emission spectrum of the phosphor $\text{In}_{1.85}(\text{WO}_4)_3:0.15\text{Eu}^{3+}$ excited at 610nm

3.3 Influence of doped Eu^{3+} concentration on the luminescence properties

Emission spectra of $\text{In}_{2-x}(\text{WO}_4)_3:x\text{Eu}^{3+}$ ($x=0.05, 0.10, 0.15, 0.20, 0.30$) phosphors with different Eu^{3+} concentrations are depicted in Fig. 5. The samples all emit red light of 611nm under the excitation of 393nm near UV light and the sites of emission peaks have few changes. That is to say, doping Eu^{3+} in the $\text{In}_2(\text{WO}_4)_3$ only brings the change of intensity.

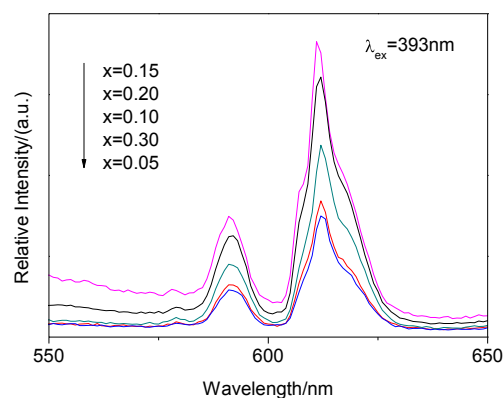


Fig. 5. The emission spectra of the $\text{In}_{2-x}(\text{WO}_4)_3:x\text{Eu}^{3+}$ phosphor with different Eu^{3+} -doped content.

The influence of doped Eu^{3+} concentration on the luminescence intensity is plotted in Fig. 6. It can be seen from the figure that the luminescence intensity reaches the maximum value only when the doped Eu^{3+} concentration is 15mol%. The low or excessive doped concentration will lead to the reduction of luminescence intensity due to the lack of luminescence ions and the appearance of concentration quenching, respectively[44]. For this reason, $\text{In}_{1.85}(\text{WO}_4)_3:0.15\text{Eu}^{3+}$ is a comparatively ideal red-emitting phosphor in the present experiment.

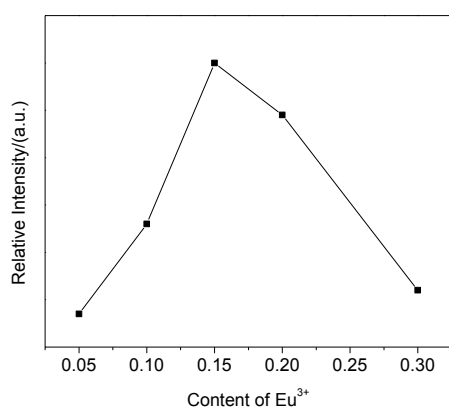


Fig. 6. The influence of content of Eu^{3+} on the photoluminescence intensity

4. Conclusions

As a whole, Eu^{3+} -doped $\text{In}_2(\text{WO}_4)_3$ phosphors were successfully obtained through a common solid-state reaction method in air. The as-synthesized phosphors have a pure phase with an orthorhombic structure and the size distribution is normal. In the excitation spectrum, the characteristic absorption peaks of Eu^{3+} at ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ (393nm) and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ (464nm) comply with the emission wavelength of near-UV or blue chip. The strongest red light emission of 611nm corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ in the emission spectrum was observed. The luminescence intensity of the phosphor reduced when the Eu^{3+} concentration exceeded 15mol% owing to concentration quenching appearance, and the optimum doping concentration was confirmed to be about 15mol%. In view of this, the phosphor $\text{In}_2(\text{WO}_4)_3:\text{Eu}^{3+}$ may become a potential candidate of red-emitting phosphor in the white LEDs application.

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