

A red-emitting phosphor for white LEDs and its luminescence properties

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A batch of phosphors $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x}:0.4\text{Eu}^{3+}$ ($x=0.02, 0.04, 0.06, 0.08, 0.10$) were synthesized by a solid-state method in high temperature air. The crystallization and luminescence properties were respectively identified by X-ray diffraction (XRD) and molecular fluorescence spectrometer. The XRD pattern shows that the phosphor has no impure phase. The excitation spectrum demonstrates that the phosphor can be efficiently excited by near UV light at 394 nm and blue light at 465 nm. The emission spectrum presents the phosphor exhibiting bright red emission at 611 nm due to the Eu^{3+} transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$. WO_4^{2-} content does not make the emission shapes and peak positions change except for the emission intensity. When x is equal to 0.04, the intensity reaches the maximum. The color coordinates are $x=0.60$ and $y=0.36$, which are close the standard red values (0.67,0.33). The results indicates that the $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96}:0.4\text{Eu}^{3+}$ may be a promising red-emitting phosphor for white LEDs.

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1. Introduction

Currently, more attention has been attracted in producing the phosphor-converted white light-emitting diodes (LEDs) because of their long performance life, high luminous efficiency and environmental- friendly feature [1-6]. At the same time, the white LEDs are thought to be a type of important solid-state light sources which can substitute some incandescent and fluorescent lamps [7-9]. Up to now, the most convenient technology to fabricate white LEDs is combining a GaN blue LED chip with a yellow-emitting phosphor ($\text{YAG}:\text{Ce}^{3+}$) [10-12]. But high color temperature and low color rendering index (CRI) exist on this kind of white LEDs thanks to the shortage of red-emitting phosphors. So, in order to improve the luminescence qualities, the white LEDs add a red-emitting ingredient on the yellow phosphor. Unfortunately the ingredient gives priority to the sulphides such as $\text{Y}_2\text{O}_2:\text{Eu}^{3+}$, which has instability, short lifetime and low efficiency [13-18]. Therefore, developing novel red-emitting phosphor is a meaningful task.

Recent years molybdates doped with trivalent europium ion (Eu^{3+}) are enjoyed by researchers due to their chemical stability and good absorption bands from the near ultraviolet (UV) to visible region. These Eu^{3+} -activated molybdates with scheelite structure have efficient red emission in near UV and blue irradiation. For example, Ru et al. synthesized red light-emitting phosphor $\text{Li}_2\text{Eu}_4(\text{MoO}_4)_7$ by a sol-gel method and the phosphor could be effectively excited by near UV light at 395 nm and blue light at 465 nm to emit strong red light at 615 nm [19]. Qiao et al. studied $\text{LiYb}_{1-x}\text{Eu}_x(\text{MoO}_4)_2$ ($x=0.01-1$) phosphor prepared by conventional solid state reaction and the

phosphor showed bright red luminescence peaking at about 618 nm under the excitation of 396 nm and 467 nm lights [20]. The present researches reveal that the Eu^{3+} ions doped with molybdates have intensive red emission owing to the effective f-f transition. Motivated by the thoughts of developing excellent phosphors used as white LEDs, a series of phosphors $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x}:0.4\text{Eu}^{3+}$ based on the previous investigation were synthesized by general solid-state method and their photoluminescence properties were also investigated [21].

2. Experimental

2.1. Synthesis

The phosphors $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x}:0.4\text{Eu}^{3+}$ were synthesized by a conventional high temperature solid-state reaction technique. The starting materials for the sample syntheses are indium oxide (In_2O_3 , 99.99%), molybdenum trioxide (MoO_3 , analytical grade), tungsten oxide (WO_3 , analytical grade) and europium oxide (Eu_2O_3 , 99.99%). Stoichiometric amounts of these original materials were weighted and mixed thoroughly in an agate mortar, then the homogeneous mixture was transferred to an alumina crucible and pre-sintered at 500 °C for 4h in an electric muffle furnace. Finally the mixture was sintered at 1000 °C for 8h and the final sample was cooled down to room temperature in air.

2.2. Characterization

The phase purity of the synthesized sample was examined by powder X-ray diffraction (XRD) using a Shimadzu diffractometer with Cu K α radiation at 40 kV and 150 mA. The excitation and emission spectra were measured by an RF-5301 molecular fluorescence spectrometer with a Xe lamp under the slit width located at 3 nm. All the above measurements were performed at room temperature in air.

3. Results and discussion

3.1. XRD characterization and size distribution

Fig. 1 illustrates the XRD images of the phosphors $\text{In}_{1.6}(\text{WO}_4)_{0.1}(\text{MoO}_4)_{2.9}:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$. The XRD peaks of the $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{WO}_4)_{0.1}(\text{MoO}_4)_{2.9}:0.4\text{Eu}^{3+}$ are similar to the Joint Committee on Powder Diffraction Standards (JCPDS) (No. 21-0908). It reveals that both of them are of single phase with a cubic crystal structure. Because of the different ionic radii among Eu^{3+} (0.107 nm), Mo^{6+} (0.041 nm) and In^{3+} (0.080 nm), the left shift of the diffraction peaks appears. However, the peak positions of the $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{WO}_4)_{0.1}(\text{MoO}_4)_{2.9}:0.4\text{Eu}^{3+}$ are the same except for the intensity of the peaks. As a result, it can be concluded that a small quantity of W added to the $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$ makes the peak positions not change and improves the degree of crystallinity which results in increasing the peak intensity.

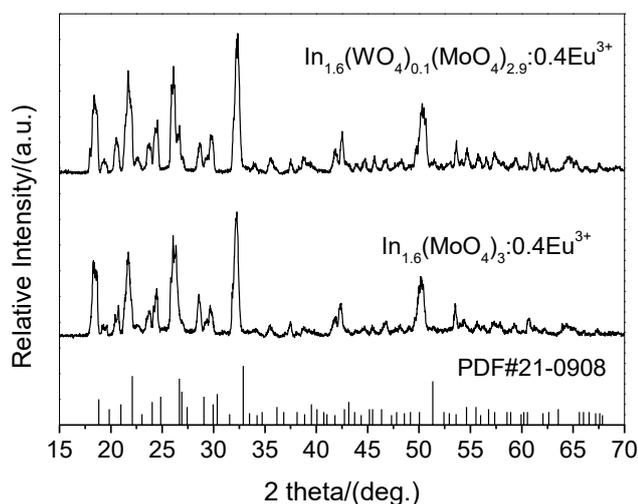


Fig. 1. X-ray diffraction patterns of the phosphors $\text{In}_{1.6}(\text{WO}_4)_{0.1}(\text{MoO}_4)_{2.9}:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$

3.2. Analysis on the excitation and emission spectra

The excitation spectra of the phosphors $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96}:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$ ($\lambda_{\text{em}}=611\text{ nm}$) are shown in Fig. 2. The both spectra have a group of sharp peaks above 350 nm, but the former is a little

stronger than the latter. These peaks correspond to the f-f transitions of Eu^{3+} and the two stronger peaks are respectively due to the transitions of the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ at 394 nm and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ at 465 nm [22-24]. The two transitions which present stronger absorption match well with the output wavelengths of near UV and blue LED chips, which indicates that the phosphor $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96}:0.4\text{Eu}^{3+}$ can be used as a kind of phosphors for the above chips in the field of white LEDs.

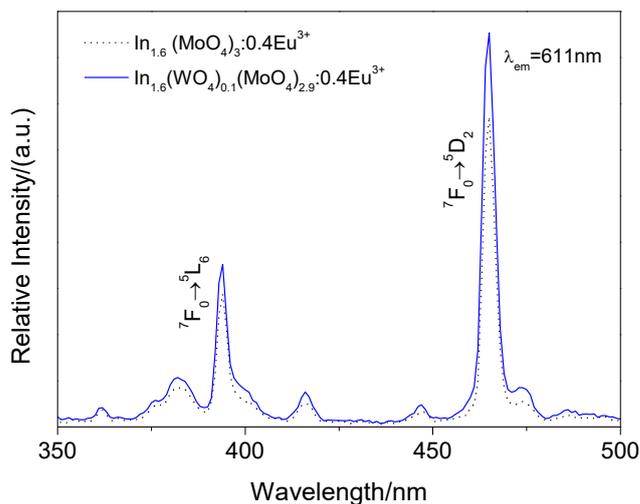


Fig. 2. Excitation spectra of the phosphors $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96}:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$

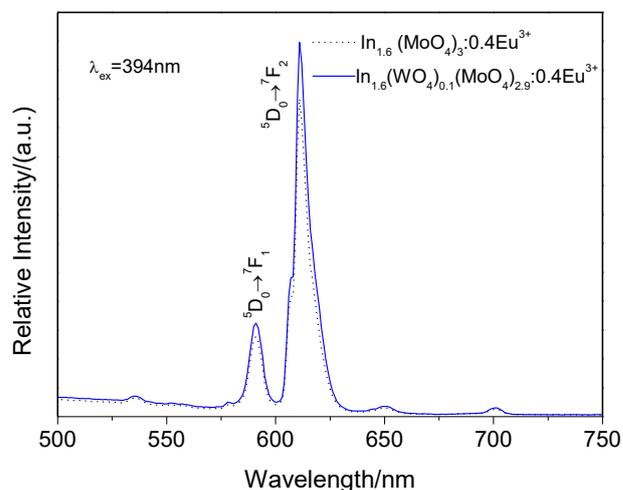


Fig. 3. Emission spectra of the phosphors $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96}:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$

Fig. 3 represents the emission spectra of the phosphors $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96}:0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$ excited at 394 nm. From the figure, it can be seen that the phosphor $\text{In}_{1.6}(\text{MoO}_4)_3:0.4\text{Eu}^{3+}$ has the stronger intensity than the phosphor $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96}:0.4\text{Eu}^{3+}$. Both of the spectra include several sharp lines in the range from 350 nm to 500 nm and the lines originate from the Eu^{3+} transitions from the excited ${}^5\text{D}_0$ state to the ground ${}^7\text{F}_J$ ($J=0, 1, 2$, etc.) states [25, 26]. Among these transitions, there are two main transitions

which are the magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ at 591 nm and the electric dipole ${}^5D_0 \rightarrow {}^7F_2$ at 611 nm. However, the Eu^{3+} transition of ${}^5D_0 \rightarrow {}^7F_2$ is much stronger than any other transition, which shows that the Eu^{3+} ions take up asymmetric cation environments in the host [27]. Therefore, the as-obtained phosphor can be a red-emitting phosphor to produce the white LEDs.

3.3. Effect of WO_4^{2-} dosage on the luminescence properties

Fig. 4 gives the luminescence properties of the phosphors $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x} \cdot 0.4\text{Eu}^{3+}$ ($x=0.02, 0.04, 0.06, 0.08, 0.10$) depending on the WO_4^{2-} content. The emission shapes and peak positions in the spectra have no distinct changes as the WO_4^{2-} content varies. Meanwhile, the emission intensity increases with the increasing of WO_4^{2-} content until x is up to 0.04. Finally, the intensity decreases owing to the occurrence of concentration quenching. Thus right amount of WO_4^{2-} in the phosphor $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x} \cdot 0.4\text{Eu}^{3+}$ can play an active role to absorb the excitation energy, then the energy is transferred to the Eu^{3+} , which brings about the excited energy of Eu^{3+} increasing and improves the emission intensity. But the superfluous WO_4^{2-} will do harmful to the emission intensity. So the $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96} \cdot 0.4\text{Eu}^{3+}$ is an optimal ingredient phosphor in this work.

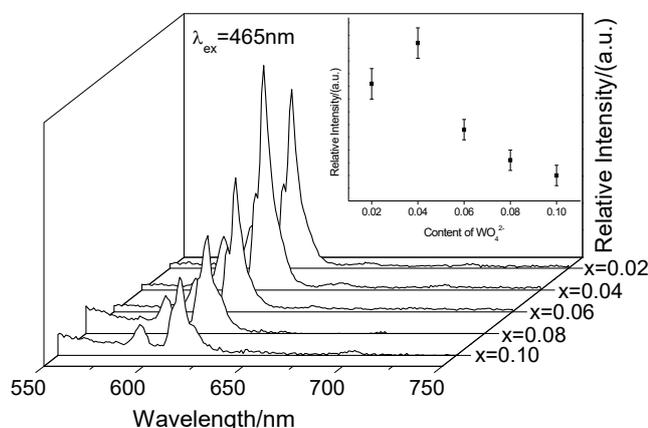


Fig. 4. Effect of WO_4^{2-} content on luminescence of the phosphors $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x} \cdot 0.4\text{Eu}^{3+}$ ($x=0.02, 0.04, 0.06, 0.08, 0.10$). The inset depicts the emission intensities of the phosphors $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x} \cdot 0.4\text{Eu}^{3+}$ as a function of the WO_4^{2-} content

Table 1 shows that the calculated CIE chromaticity coordinates of the phosphors $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96} \cdot 0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3 \cdot 0.4\text{Eu}^{3+}$ excited at 394 nm. The color coordinates of the two phosphors are near to the standard red coordinates which are $x=0.67$ and $y=0.33$. That is to say, the obtained samples are the ideal red-emitting phosphor.

Table 1. CIE chromaticity coordinates and relative emission intensity of ${}^5D_0 \rightarrow {}^7F_2$ for $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96} \cdot 0.4\text{Eu}^{3+}$ and $\text{In}_{1.6}(\text{MoO}_4)_3 \cdot 0.4\text{Eu}^{3+}$ excited at 394 nm

| Phosphor | ${}^5D_0 \rightarrow {}^7F_2$ intensity | CIE coordinates | |
|--|--|-----------------|------|
| | | x | y |
| $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96} \cdot 0.4\text{Eu}^{3+}$ | 648 | 0.60 | 0.36 |
| $\text{In}_{1.6}(\text{MoO}_4)_3 \cdot 0.4\text{Eu}^{3+}$ | 550 | 0.62 | 0.35 |

4. Conclusions

In conclusion, red-emitting phosphors $\text{In}_{1.6}(\text{WO}_4)_x(\text{MoO}_4)_{3-x} \cdot 0.4\text{Eu}^{3+}$ ($x=0.02, 0.04, 0.06, 0.08, 0.10$) were synthesized by a general solid-state reaction technique in high temperature atmosphere. The phosphors have a cubic crystal structure with a single phase. The excitation spectrum shows that the phosphor can be effectively excited by 394 nm or 465 nm light and the emission spectrum represents the phosphor emitting intensive red light at 611 nm owing to the electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ of the Eu^{3+} . WO_4^{2-} content does not change the emission shapes and peak positions. With the increasing of the WO_4^{2-} content, at the beginning the emission intensity increases and at last it decreases. The CIE chromaticity coordinates of the phosphor $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96} \cdot 0.4\text{Eu}^{3+}$ excited at 394 nm are $x=0.60$ and $y=0.36$, which are close to the standard red vules (0.67,0.33). Hence, the phosphor $\text{In}_{1.6}(\text{WO}_4)_{0.04}(\text{MoO}_4)_{2.96} \cdot 0.4\text{Eu}^{3+}$ is suggested to be a potential red-emitting material for white LEDs.

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