

Preparation of $\text{Sr}_{0.88-1.5x}\text{MoO}_4:0.08\text{Eu}^{3+}, x\text{Sm}^{3+}$ red-emitting phosphors by hydrothermal method and their luminescence properties through energy transfer

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A series of red-emitting phosphors $\text{Sr}_{0.88-1.5x}\text{MoO}_4:0.08\text{Eu}^{3+}, x\text{Sm}^{3+}$ have been synthesized by hydrothermal method. The phosphors have the advantages of narrower particle size distribution and regular homogeneous shape. The luminescent properties of the phosphors were systematically studied. The introduction of Sm^{3+} into the red-emitting phosphors can generate a strong excitation line at 405 nm, originating from the ${}^6\text{H}_{5/2} \rightarrow {}^4\text{K}_{11/2}$ transition of Sm^{3+} , significantly extending the excitation region for matching the near-ultraviolet light-emitting diodes (~400 nm). Energy transfer from Sm^{3+} to Eu^{3+} was observed. When the mole fraction of Sm^{3+} is 2%, the emission intensity of red light excited at 405 nm is the strongest.

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1. Introduction

As the most challenging application to replace traditional incandescent and fluorescent lamps, white light LEDs have particularly received much attention. For the way of phosphor conversion, the red/green/blue tricolor phosphors are pumped by UV-InGaN chips (~400 nm) or blue GaN chips (~460 nm) and generate white light [1]. However, the efficiency of the $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ is unstable due to the release of sulfide gas, and is much lower than that of the blue and green phosphors [2]. Based on blue LED plus yellow phosphor, there exist at least two drawbacks, such as lower color-rendering index and lower luminous efficiency [3]. So that red-emitting phosphor is introduced to improve the CRI and increase the light conversion efficiency [4]. Therefore, it is crucial to seek alternative red phosphors with high luminescence and satisfactory chemical stability.

Recently, Eu^{3+} -doped molybdates and tungstates phosphors have been extensively investigated as red phosphors. The intensities of Eu^{3+} at around 394 and 465nm are enhanced obviously in these materials compared with other most Eu^{3+} -doped phosphors [5–8]. However, most of these materials were prepared by traditional solid-state method, which usually requires high temperatures, lengthy heating process and subsequent

grinding. The grinding process damages the phosphor surfaces, resulting in the loss of emission intensity. In addition, the aggregation and inhomogeneous shape are also unavoidable, which inhibit the absorption of the excitation energy and therefore reduce the emission intensity [9]. Therefore, a simple and economical method for making high-quality phosphor is desirable. Hydrothermal method has some advantages over the conventional solid-state reaction method, including good homogeneity, lower calcinations temperature and the prepared samples show a small size and narrow particle size distribution. In this paper, we report the preparation and luminescent properties of $\text{Sr}_{0.88-1.5x}\text{MoO}_4:0.08\text{Eu}^{3+}, x\text{Sm}^{3+}$ by hydrothermal method. The energy transfer between Sm^{3+} and Eu^{3+} is mainly studied by analyzing the change of excitation spectra.

2. Experimental

The red-emitting phosphors $\text{Sr}_{0.88-1.5x}\text{MoO}_4:0.08\text{Eu}^{3+}, x\text{Sm}^{3+}$ were synthesized by hydrothermal method. The detail of reaction procedure is as follows: $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was used to offer MoO_4^{2-} , and it was prepared by adding $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (A.R) into deionized water. Meanwhile, $\text{Sr}(\text{NO}_3)_2$ was solved in deionized

water to be $\text{Sr}(\text{NO}_3)_2$ solution. Then, the dopant ions were added into $\text{Sr}(\text{NO}_3)_2$ solution by dropping appreciated $\text{Eu}(\text{NO}_3)_3$ or $\text{Sm}(\text{NO}_3)_3$ solution, which was prepared in advance. The Na_2MoO_4 solution was dropped into $\text{Sr}(\text{NO}_3)_2:\text{Eu}^{3+}$, Sm^{3+} solution slowly under vigorous stirring. A white precipitate was observed in the glass beaker. The vigorous stirring was continued for 30 min. Finally, the precursor solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was subsequently sealed and maintained at 180°C for 12h. After that, the autoclave was cooled to room temperature naturally. The precursors was collected by filtering, washing and drying. Then, the precursors was sintered in a high temperature furnace in the air at 800°C for 2 h, the red-emitting phosphors can were obtained.

The structures of the products were characterized by X-ray powder diffraction (XRD) employing $\text{CuK}\alpha$ radiation at 40 kV and 250 mA. A step size of 0.02° (2θ) was used with a scan speed of $4^\circ/\text{min}$. The morphology was investigated by using scanning electron microscopy (SEM) (JSM-6360LV). Excitation and emission spectra were measured by using a Hitachi F-4600 spectrometer equipped with a 150W xenon lamp under a working voltage of 500 V. The excitation and emission slits were set at 2.5 nm and scanning speed was 1200 nm/min.

3. Results and discussion

The XRD pattern of the $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}$, 0.02Sm^{3+} sample is presented in Fig. 1. Compared with the JCPDS card 27-0841, All diffraction peaks index well to the rhombohedral phase structure of SrMoO_4 . The results indicate that a little amount of added Eu^{3+} and Sm^{3+} has almost no influence on the host structure and no impurities are observed in the resulting product.

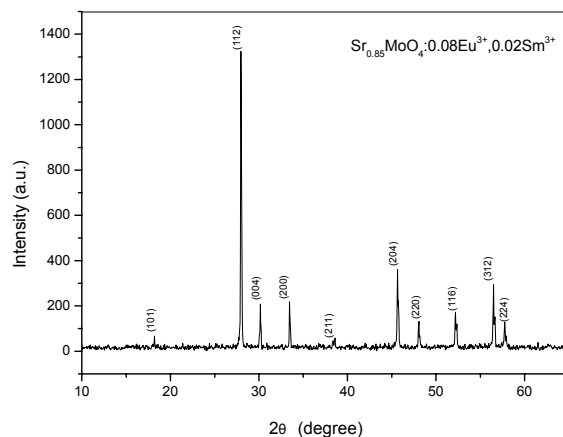


Fig. 1. X-ray diffraction patterns of phosphor

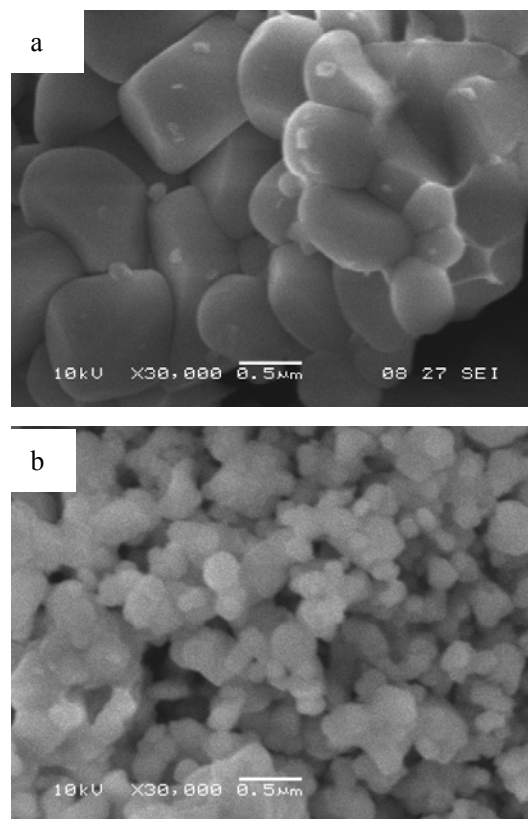
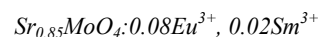


Fig. 2. SEM photographs of $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}$, 0.02Sm^{3+} phosphors prepared by (a) solid-state method and (b) hydrothermal method.

During the application of phosphors in LED, the size distribution and shape of the phosphors are important, so the SEM photographs of the red phosphors $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ prepared by the solid state reaction (a) and hydrothermal method (b) are shown in Fig. 2. For the samples with hydrothermal method, the particle size distribution is narrower, and the shapes of the samples are regular and homogeneous in comparison with those of samples produced by solid-state method, which is in favor of fabrication of the solid-state lighting devices and can better meet the application of phosphors in LED.

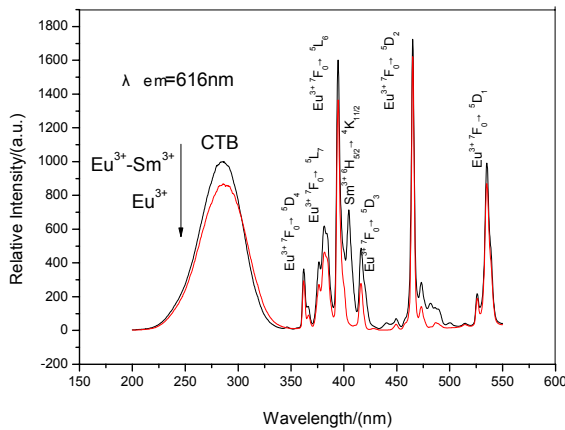


Fig. 3. The excitation spectra of $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ ($\text{Eu}^{3+}\text{-Sm}^{3+}$) and $\text{Sr}_{0.88}\text{MoO}_4:0.08\text{Eu}^{3+}$ (Eu^{3+}) under 616 nm.

The excitation spectra of $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ and $\text{Sr}_{0.88}\text{MoO}_4:0.08\text{Eu}^{3+}$ are shown in Fig. 3. The excitation spectra monitoring the red emission line at 616 nm are composed of an intense broad band and some sharp lines. The broad band in the range of 200-350 nm is assigned to the combination of the charge-transfer transition of $\text{O}^{2-} \rightarrow \text{Mo}^{6+}$ and $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$. The sharp peak around 405 nm corresponds to the ${}^6\text{H}_{5/2} \rightarrow {}^4\text{K}_{11/2}$ transition of Sm^{3+} , and the appearance of the 405 nm excitation line indicates the performance of energy transfer from Sm^{3+} to Eu^{3+} . The other sharp peaks located at wavelengths longer than 350 nm are due to the intra-configurational f-f transitions of Eu^{3+} , including the peak at ~ 362 nm attributed to ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, the peaks at ~ 381 nm attributed

to ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$, the peak at ~ 395 nm attributed to ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, the peak at ~ 465 nm attributed to ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$, and the peak at ~ 535 nm attributed to ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, respectively. Among them, the peaks at ~ 395 nm and 405 nm are close to the emission peak situation of near-UV chips (390-410 nm). It is implied that the phosphor can be effectively excited by radiation with wavelength lying in the near-UV zone.

Fig. 4 displays the normalized emission spectra of $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$, $\text{Sr}_{0.88}\text{MoO}_4:0.08\text{Eu}^{3+}$ and $\text{Sr}_{0.97}\text{MoO}_4:0.02\text{Sm}^{3+}$ phosphors excited at different wavelength. The emission spectrum of $\text{Sr}_{0.97}\text{MoO}_4:0.02\text{Sm}^{3+}$ excited at 405 nm is shown in Fig. 4a, the main peaks of Sm^{3+} at ~ 561 , ~ 596 -604 and ~ 642 nm corresponding to the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$, ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ and ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ transitions, respectively. In Fig. 4b and 4c, there are several strong and sharp peaks which are attributed to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J=1, 2, 3, 4$) charge transitions, indicating the existence of Eu^{3+} ions in the $\text{Sr}_{0.88}\text{MoO}_4:0.08\text{Eu}^{3+}$ and $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ matrices.

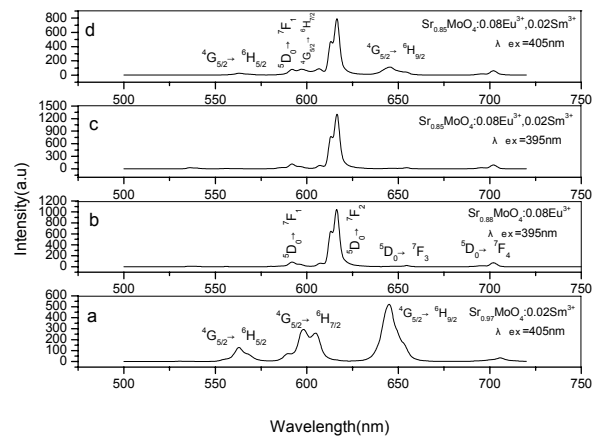


Fig. 4. The emission spectra of $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$, $\text{Sr}_{0.88}\text{MoO}_4:0.08\text{Eu}^{3+}$ and $\text{Sr}_{0.97}\text{MoO}_4:0.02\text{Sm}^{3+}$ excited at different wavelength.

The spectra consist of well resolved features at ~ 591 , ~ 616 , ~ 655 , and ~ 703 nm, which can be assigned to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$, respectively. Due to the shielding effect of 4f electrons by 5s and 5p, emission peaks are expected, consistent with the sharp and intense peak around 616 nm which is due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, based on selection rules. But the main emission peaks of Sm^{3+} are not observed in Fig. 4c. It is implied that Sm^{3+} cannot be effectively excited by

395nm, and there isn't the occurrence of efficient energy transfer from Eu^{3+} ions to Sm^{3+} ions. Characteristic emission peaks of Eu^{3+} were observed in the emission spectra of $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ phosphors excited at 405 nm (Figure 4d). Meanwhile, the emission of Sm^{3+} ions also appear excited at 405 nm. It means the occurrence of efficient energy transfer from Sm^{3+} ions to Eu^{3+} ions. Thus, the emission of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J=1, 2, 3, 4$) transition of Eu^{3+} ions was observed.

The emission spectra of $\text{Sr}_{0.88-1.5x}\text{MoO}_4:0.08\text{Eu}^{3+}, x\text{Sm}^{3+}$ ($x=0.01, 0.02, 0.03, 0.04, 0.05$) excited at 405 nm are shown in Figure 5. In SrMoO_4 , the concentration of Eu^{3+} ions was fixed at 8%, and the concentrations of Sm^{3+} ranged from 1 to 5%. The emission peaks at 616 nm grow with the increasing of the Sm^{3+} concentrations up to 2% and then decrease as the Sm^{3+} concentration beyond 2%. When the mole fraction of Sm^{3+} is 2%, the emission intensity of red light excited at 405 nm is the strongest.

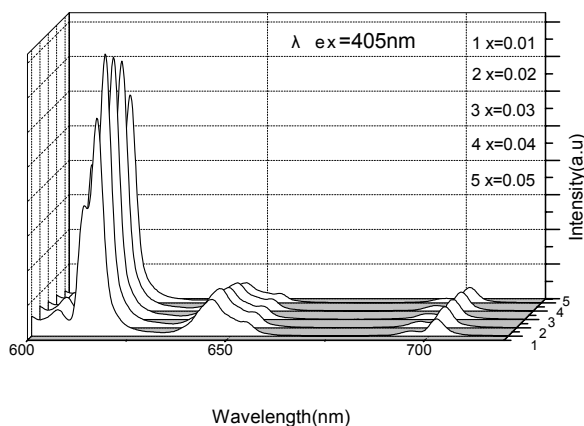


Fig. 5. The emission spectra of $\text{Sr}_{0.88-1.5x}\text{MoO}_4:0.08\text{Eu}^{3+}, x\text{Sm}^{3+}$ ($x=0.01, 0.02, 0.03, 0.04, 0.05$) excited at 405 nm.

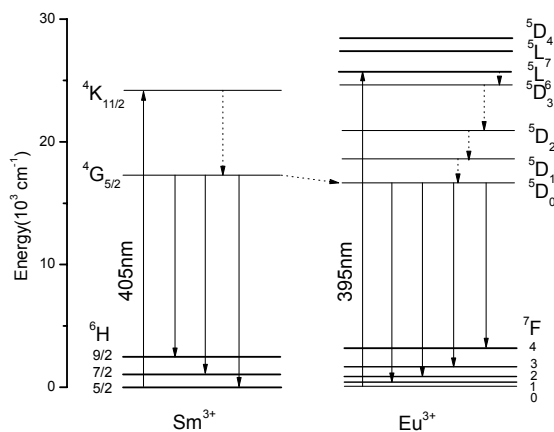


Fig. 6. Excitation, energy transfer, and emission processes of Sm^{3+} and Eu^{3+} in the $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ phosphor.

A diagram of Fig. 6 shows how the rare earth ions in the $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ phosphor absorb energy (near-UV light) and emit a red light. If the $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ phosphor is excited by 395nm corresponding to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ of Eu^{3+} , the Eu^{3+} ion absorbs energy by itself and the energy state moves to the lowest excited energy-level (${}^5\text{D}_0$) through relaxation. Finally, a red emission occurs through the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transition. On the other hand, if the $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ phosphor is excited by 405nm corresponding to the ${}^6\text{H}_{5/2} \rightarrow {}^4\text{K}_{11/2}$ of Sm^{3+} , the Sm^{3+} ion absorbs energy and the energy state moves to the lowest excited energy-level (${}^4\text{G}_{5/2}$) through relaxation. The Sm^{3+} transfers this energy to the ${}^5\text{D}_0$ state of Eu^{3+} without any red emission. Therefore, the red emission due to Eu^{3+} occurs through the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transition and emission due to Sm^{3+} is not observed.

4. Conclusions

In conclusion, the red-emitting phosphor $\text{Sr}_{0.88-1.5x}\text{MoO}_4:0.08\text{Eu}^{3+}, x\text{Sm}^{3+}$ has been obtained successfully by hydrothermal method. The red fluorescence of Eu^{3+} and energy transfer from Sm^{3+} to Eu^{3+} in all the products were observed. Owing to efficient energy transfer, a strong excitation line at 405 nm, originating from ${}^6\text{H}_{5/2} \rightarrow {}^4\text{K}_{11/2}$ transition of Sm^{3+} , is generated in the excitation spectra of the Eu^{3+} fluorescence. It significantly extends the excitation region of these materials for matching the near-ultraviolet light-emitting diodes (~ 400 nm). For the aim to use in W-LEDs with high color rendering index and color reproducibility, it is investigated that the red phosphors $\text{Sm}^{3+}\text{-Eu}^{3+}$ codoped $\text{Sr}_{0.85}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.02\text{Sm}^{3+}$ is an excellent red-emitting phosphor for LED.

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