

Luminescence and energy transfer in the red-emitting phosphor system $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$

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The red-emitting phosphor $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ has been prepared via hydrothermal method. The luminescent properties of the phosphor and energy transfer from Tb^{3+} to Eu^{3+} are investigated. The luminescence properties of Eu^{3+} ions in $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ could be evidently improved by co-doping of Tb^{3+} ions, which was due to the efficient energy transfer process from Tb^{3+} to Eu^{3+} ions. The chromaticity coordinates of $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ is closer to the standard red than that of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$.

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1. Introduction

Because white light emitting diode had the advantages of high efficiency, long lifetime, fast response, safety and environmental protection, it has attracted more and more attention [1, 2]. Recently phosphor-converted (pc) method is the most common to fabricate white LED [3]. As the important ingredient in pc-white LED, Phosphor affects the development and application of white LED directly. Because of limitation of red phosphors applied nowadays, especially to the properties of red phosphor excited by blue and UV light, which can affect directly the color rendering of white LED, In addition, the commercial phosphors are generally prepared by conventional high temperature solid state reaction which gradually cannot meet the demand of development in the area of light and display because of energy-consuming and uncontrollable for the shape of particles [4-9]. Therefore, it is great meaningful to develop new good properties of red-emitting phosphors and propose a novel energy-saving way for the preparation of phosphors.

Due to the good heat and chemical stability of rare earth molybdate emitting materials, the rare earth molybdate emitting material is a kind of very good emitting substrate materials and is presently the hotspot of research of the red phosphors for LED [10, 11]. In this paper, the hydrothermal method is chosen to prepare the red phosphor $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$. The emitting behaviour of phosphor is discussed, and the energy transfer between Eu^{3+} and Tb^{3+} is mainly studied in $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$.

2. Experimental

The red-emitting phosphor $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ was prepared by hydrothermal method. The 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, $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Ca}, \text{Sr}$) was solved in deionized water to be $\text{M}(\text{NO}_3)_2$ solution. Then, the dopant ions were added into $\text{M}(\text{NO}_3)_2$ solution by dropping appreciated $\text{Eu}(\text{NO}_3)_3$ or $\text{Tb}(\text{NO}_3)_3$ solution, which was prepared in advance. The Na_2MoO_4 solution was dropped into $\text{M}(\text{NO}_3)_2:\text{Eu}^{3+}, \text{Sm}^{3+}$ 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 precursor 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. The

chromaticity coordinate is tested with Model No. PMS-50 ultraviolet-visible-infrared spectrum analysis system.

3. Results and discussion

The XRD pattern of the $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ sample is presented in Fig. 1. Compared with the JCPDS card 29-0351, all diffraction peaks index well to the tetragonal crystal phase structure of CaMoO_4 . The results indicate that a little amount of added Eu^{3+} , Sr^{2+} and Tb^{3+} has almost no influence on the host structure and no impurities are observed in the resulting product.

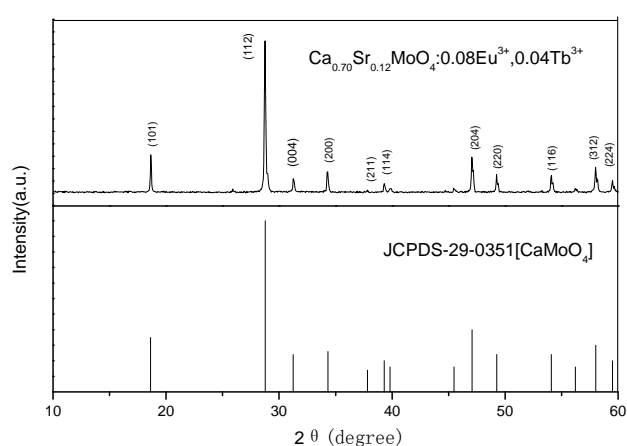


Fig. 1. XRD of $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$.

The SEM photographs of the red phosphor $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ prepared by hydrothermal method is shown in Fig. 2. The particle size distribution is narrower and the average sizes of particles are 0.6-0.9 μm in diameter without aggregating. The morphologies of the samples are spherical, and the shapes of the samples are regular and homogeneous, which is in favor of fabrication of the solid-state lighting devices and can better meet the application of phosphors in LED.

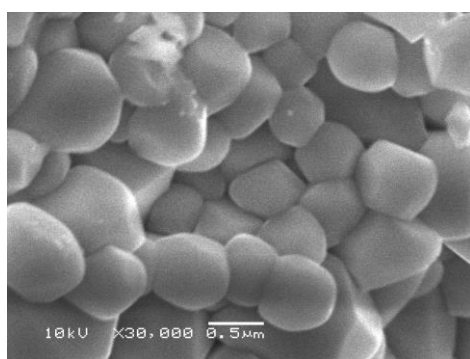


Fig. 2. SEM photographs of $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ phosphor prepared by hydrothermal method.

The excitation spectra of $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ is 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 other sharp peaks located at wavelengths longer than 350 nm are due to the f-f transitions of Eu^{3+} and Tb^{3+} , the f-f transitions of Eu^{3+} in excitation spectrum include sharp lines ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$ at ~ 362.4 nm, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$ at ~ 382.0 nm, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ at ~ 394.8 nm, and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ at ~ 465.4 nm. The f-f transitions of Tb^{3+} sharp lines ${}^7\text{F}_6 \rightarrow {}^5\text{D}_2$ at ~ 367.0 nm and ${}^7\text{F}_0 \rightarrow {}^5\text{L}_7$ at ~ 376.6 nm. The wavelengths at ~ 394.8 nm and 465.4 nm are nicely in agreement with the widely applied UV or blue output wavelengths of GaN-based LED chips.

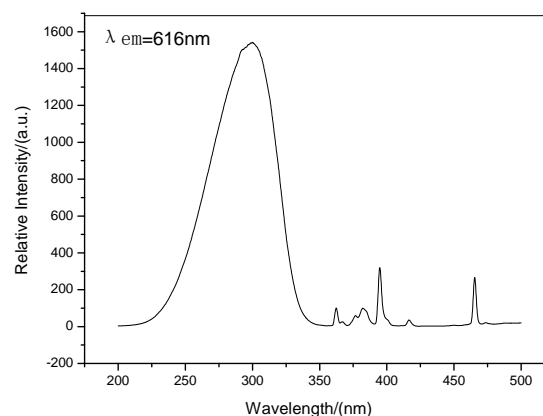


Fig. 3. The excitation spectra of $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$.

Fig. 4 displays the normalized emission spectra of $\text{Ca}_{0.70}\text{Sr}_{0.24}\text{MoO}_4:0.04\text{Tb}^{3+}$ (a), $\text{Ca}_{0.70}\text{Sr}_{0.18}\text{MoO}_4:0.08\text{Eu}^{3+}$ (b) and $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ (c) phosphors excited at 287 nm. In the emission spectrum of $\text{Ca}_{0.70}\text{Sr}_{0.24}\text{MoO}_4:0.04\text{Tb}^{3+}$ (a), the main peaks of Tb^{3+} at ~ 489 , ~ 545 , 584 and ~ 616 nm corresponding to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$, ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$ transitions, respectively. Among them, the peak of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ at 545 nm is the strongest. In the emission spectrum of $\text{Ca}_{0.70}\text{Sr}_{0.18}\text{MoO}_4:0.08\text{Eu}^{3+}$ (b), the spectra consist of well resolved features at ~ 540 , ~ 591 , ~ 616 , ~ 655 , and ~ 703 nm, which can be assigned to ${}^5\text{D}_1 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$, 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. Eu^{3+} - Tb^{3+} co-doped $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ (c) is worth concerning. Characteristic emission peaks of Eu^{3+} were observed in the emission spectra. Meanwhile, the emission peaks of Sm^{3+} ions also appear. But the main peaks of Tb^{3+} at ~ 489 and ~ 545 nm weaken to a certain degree, and the peaks of Tb^{3+} at ~ 584 and ~ 616 nm are covered by the

peaks of Eu^{3+} . Furthermore, Eu^{3+} - Tb^{3+} co-doped this system can improve its luminescent properties. Which mean the occurrence of efficient energy transfer from Tb^{3+} to Eu^{3+} . 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.

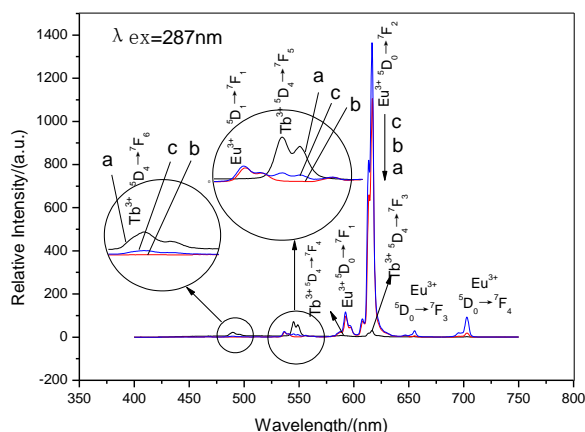


Fig. 4. The emission spectra of $\text{Ca}_{0.70}\text{Sr}_{0.24}\text{MoO}_4:0.04\text{Tb}^{3+}$ (a), $\text{Ca}_{0.70}\text{Sr}_{0.18}\text{MoO}_4:0.08\text{Eu}^{3+}$ (b) and $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ (c).

A diagram of Fig. 5 shows how the rare earth ions in the $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ phosphor absorb energy and emit a red light. The energy transfer pathway from Tb^{3+} to Eu^{3+} is from ${}^5\text{D}_4$ level of Tb^{3+} to ${}^5\text{D}_1$ level of Eu^{3+} , then it will relax to the ${}^5\text{D}_0$ level of Eu^{3+} , and go to the ground state ${}^7\text{F}_2$ by emitting a photon.

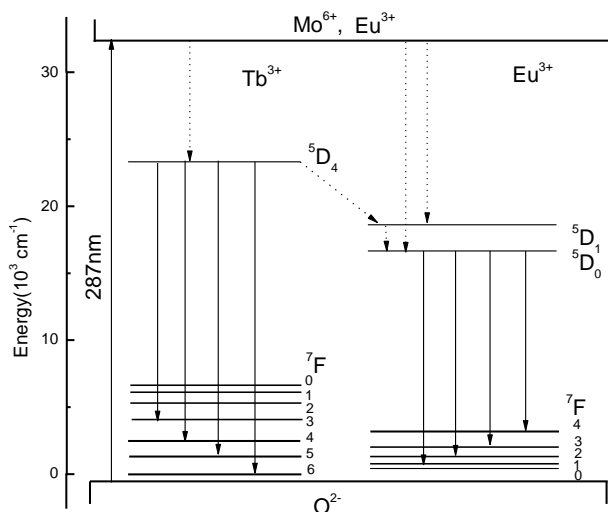


Fig. 5. Energy transfer and emission processes of Tb^{3+} and Eu^{3+} in the $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ phosphor.

The chromaticity coordinates for $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ is (0.653, 0.330), which is closer to the standard red than that of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (0.625, 0.338) [12], and is closer to the standard values of International chromaticity coordinates (0.67, 0.33). So the

$\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ show good potential of the red commercialization phosphors.

4. Conclusions

In conclusion, the red-emitting phosphor $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ has been prepared successfully by hydrothermal method. The red fluorescence of Eu^{3+} and energy transfer from Tb^{3+} to Eu^{3+} in all the products were observed. The energy transfer pathway from Tb^{3+} to Eu^{3+} is from ${}^5\text{D}_4$ level of Tb^{3+} to ${}^5\text{D}_1$ level of Eu^{3+} , then it will relax to the ${}^5\text{D}_0$ level of Eu^{3+} . The chromaticity coordinates of $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ is closer to the standard red than that of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, and is closer to the standard values of International chromaticity coordinates. For the aim to use in W-LEDs with high color rendering index and color reproducibility, it is investigated that the red phosphors Tb^{3+} - Eu^{3+} co-doped $\text{Ca}_{0.70}\text{Sr}_{0.12}\text{MoO}_4:0.08\text{Eu}^{3+}, 0.04\text{Tb}^{3+}$ is an excellent red-emitting phosphor for LED.

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References

- [1] S. Nakamura, G. F. Berlin: Springer-Verlag, 1997.
- [2] M. Thomas, P. P. Rao, M. Deepa, M. R. Chandran, P. Koshy, J Solid State Chem **182**, 203 (2009).
- [3] A. Zukauskas, R. Vaicekaskas, F. Ivanauskas, et al. Applied Physical Letters, **80**(2), 234 (2002).
- [4] H. He, X. F. Song, R. L. Fu, et al. Journal of Alloys and Compounds, **493**(1-2), 401(2010).
- [5] L. Xiao, M. Sun, J. Y. Zhang, et al. Journal of Rare Earths, **28**(1), 150(2010).
- [6] N. Kisliitsyn Mikhail, Yaroslavtsev Andrew B. Solid State Ionics, **162-163**, 197 (2003).
- [7] J. Jankowski, G. Thomas, Perier Camby L. Solid State Ionics, 101-103, 1321 (1997).
- [8] Mitsuyasu Hidemi, Nonaka Yasushi, Eguchi Koichi, Solid State Ionics, 113-115, 279 (1998).
- [9] K. Eguchi, N. Akasaka, H. Mitsuyasu, et al. Solid State Ionics, **135**(1-4), 589 (2000).
- [10] H. Liao, Y. Wang, X. Liu, et al. Chem. Mater., **12**, 2819 (2000).
- [11] C. S. Xi, Y. Z. Gao, P. Wang: Chin. J. Lumin, **31**(3), 311 (2010) (in Chinese).
- [12] Y. Pan, Q. Su, H. Xu, et al. J. Solid State Chem., **174**, 69-73 (2003).

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