Appl Phys B (2012) 107:177–181
DOI 10.1007/s00340-012-4916-x

Applied Physics B
Lasers and Optics

Luminescence properties and energy transfer process of Sm^{3+}–Eu^{3+} co-doped molybdate red-emitting phosphors by hydrothermal method

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Received: 19 August 2011 / Published online: 22 February 2012
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Abstract Eu^{3+} and Sm^{3+} co-doped molybdate phosphors have been synthesized via hydrothermal method. The phosphors have the advantages of narrower particle size distribution and regular homogeneous shape. The luminescent properties of the molybdate 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 ${}^6H_{5/2} \rightarrow {}^4K_{11/2}$ 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.

1 Introduction

White light emitting diodes (W-LEDs) have attracted great attention in the area of solid-state lighting because of their high luminous efficiency, long lifetime, low environmental impact, and small structure type [1, 2]. Currently, most commercially available W-LEDs are based on the phosphor-converted emission process [3, 4]. The most common and convenient method to generate a W-LED is to combine a blue LED with a yellow-emitting phosphors, which has low color rendering index (CRI) because of lack of red component in their spectra [5]. So another way of obtaining white LEDs is sought out, utilizing a near-UV LED chip combined with phosphors including red, green and blue emitting phosphors designed to convert the UV light to visible light [6]. Similarly, the red-emitting phosphors for W-LEDs are also essential. Therefore, the search for a stable red-emitting phosphor with a high absorption in the near-ultraviolet or blue spectral region is consequently an attractive and challenging research assignment.

The emission of Eu^{3+} ion consists usually of lines in the red spectral area, which are ascribed to the ${}^5D_0$–${}^7F_J$ ($J = 0$, 1, 2, 3, 4, 5 and 6) transitions. The red light emitting phosphor of Eu^{3+}-doped material has found an important application in the lighting and displays. More significantly, it has effective and intrinsic absorption due to the 4f–4f transition of Eu^{3+} [7].

Molybdates are being considered as good hosts for luminescent materials due to their excellent thermal and chemical stability [8, 9]. Up to now, many investigations on Eu^{3+}-doped molybdate phosphors have been reported, but most of them were synthesized by a conventional solid-state reaction route, which usually requires high temperature, time-consuming heat treatment process, subsequent product grinding [10, 11]. The grinding damages the phosphor surfaces, resulting in an emission intensity loss. Therefore, a simple method for high-quality phosphors is desirable technologically. Hydrothermal synthesis method is one of the most important "soft chemistry" techniques for the synthesis of phosphor materials with higher uniformity in particle size distribution, non-agglomeration. In this paper, we report the preparation and luminescent properties of $Ca_{0.70}Sr_{0.135}MoO_4$:$0.08Eu^{3+}$, $0.03Sm^{3+}$ via hydrothermal method. The energy transfer between Sm^{3+} and Eu^{3+}

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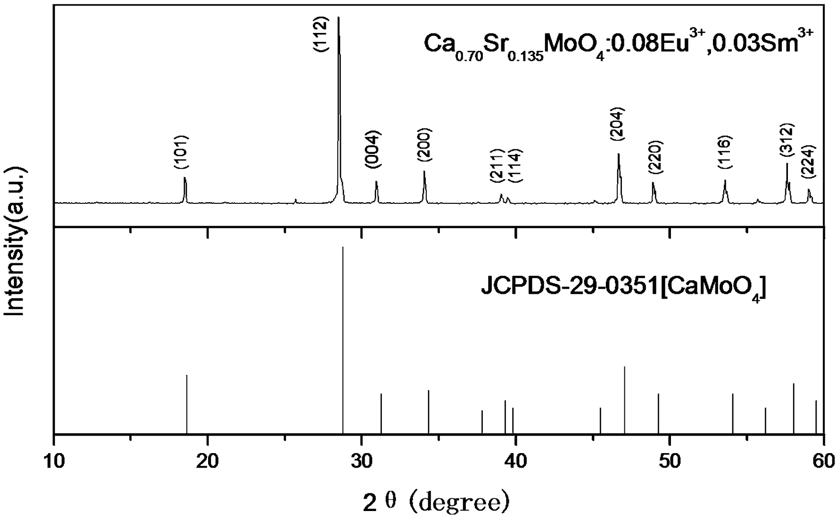

Fig. 1 X-ray diffraction patterns of phosphor $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+}

is mainly studied by analyzing the change of excitation spectra.

2 Experimental

The red-emitting phosphors were synthesized via hydrothermal method. The detail of reaction procedure is as follows: $Na_2MoO_4 \cdot 2H_2O$ was used to offer MoO_4^{2-}, and it was prepared by adding $Na_2MoO_4 \cdot 2H_2O$(A.R) into de-ionized water. Meanwhile, $M(NO_3)_2$ (M = Ca, Sr) was solved in deionized water to be $M(NO_3)_2$ solution. Then, the dopant ions were added into $M(NO_3)_2$ solution by dropping appreciated $Eu(NO_3)_3$ or $Sm(NO_3)_3$ solution, which was prepared in advance. The Na_2MoO_4 solution was dropped into $M(NO_3)_2$: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 12 h. After that, the autoclave was cooled to room temperature naturally. The precursor was collected by filtering , washing and drying. Then, the precursor was sintered in a high temperature furnace in the air at 800°C for 2 h, and the red-emitting phosphors were obtained.

The structures of the products were characterized by X-ray powder diffraction (XRD) employing CuKα radiation at 40 kV and 250 mA. A step size of 0.02° (2θ) was used with a scan speed of 4°/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 150-W 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 $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} sample is presented in Fig. 1. Compared with the JCPDS card 29-0351, only a single phase belonged to the $CaMoO_4$:Eu^{3+} is observed and no extraneous phase is emerged. According to the JCPDS card 29-0351, $CaMoO_4$ has a tetragonal crystal structure with space group of $I41/a$ (88), and its lattice parameters are $a = 0.5226$ nm, $c = 1.143$ nm, while the corresponding lattice parameters of the sample in Fig. 1 are as follows: $a = 0.5264$ nm, $c = 1.1528$ nm. It is concluded that the doping of Sr ion has increased the lattice parameters of the phosphor because of Sr^{2+} (0.113 nm) substituting Ca^{2+} (0.099 nm).

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 $Ca_{0.70}Sr_{0.135}MoO_4$: 0.08Eu^{3+}, 0.03Sm^{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.

The excitation spectra of $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} and $Ca_{0.70}Sr_{0.18}MoO_4$:0.08Eu^{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 transitions of $O^{2-} \to Mo^{6+}$ and $O^{2-} \to Eu^{3+}$. The sharp peak around 405 nm corresponds to the $^6H_{5/2} \to {}^4K_{11/2}$ 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

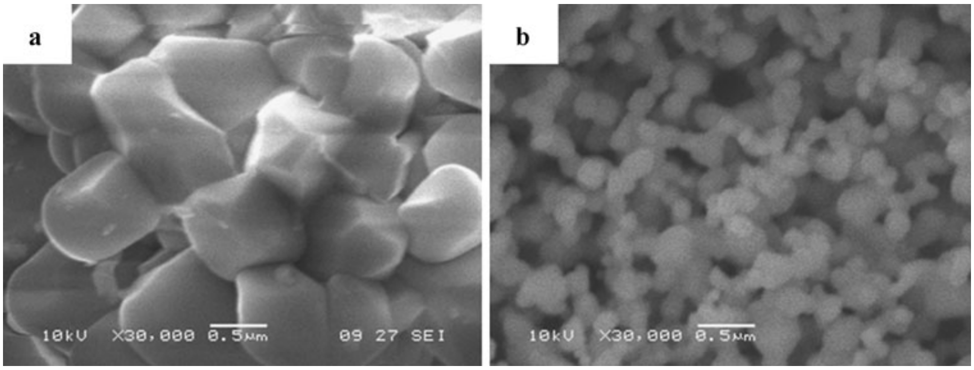

Fig. 2 SEM photographs of $Ca_{0.70}Sr_{0.135}MoO_4$:$0.08Eu^{3+}$, $0.03Sm^{3+}$ phosphors prepared by (**a**) solid-state method and (**b**) hydrothermal method

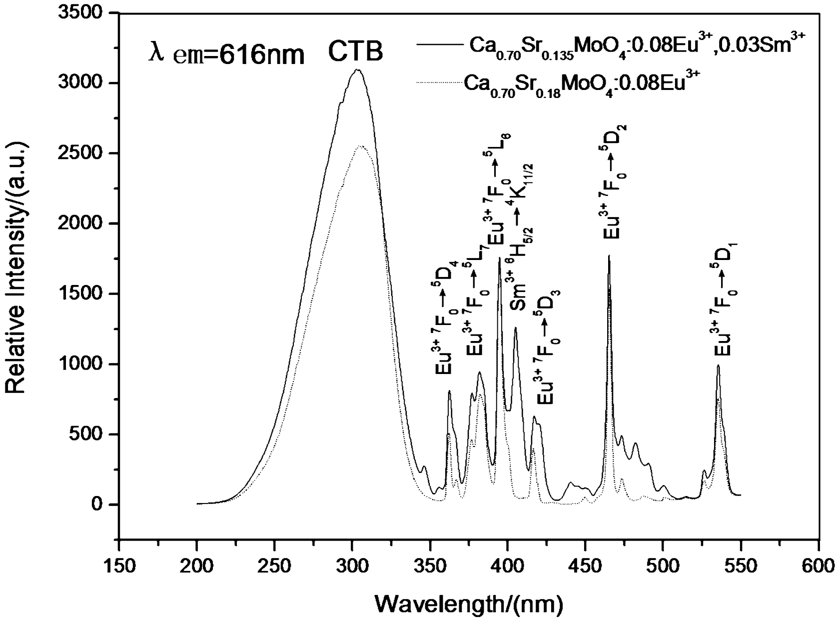

Fig. 3 The excitation spectra of $Ca_{0.70}Sr_{0.135}MoO_4$:$0.08Eu^{3+}$, $0.03Sm^{3+}$ and $Ca_{0.70}Sr_{0.18}MoO_4$:$0.08Eu^{3+}$ under 616 nm

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 $^7F_0 \rightarrow {}^5D_4$, the peaks at ~381 nm attributed to $^7F_0 \rightarrow {}^5L_7$, the peak at ~395 nm attributed to $^7F_0 \rightarrow {}^5L_6$, the peak at ~465 nm attributed to $^7F_0 \rightarrow {}^5D_2$, and the peak at ~535 nm attributed to $^7F_0 \rightarrow {}^5D_1$, 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.

Figure 4 displays the normalized emission spectra of $Ca_{0.70}Sr_{0.135}MoO_4$:$0.08Eu^{3+}$, $0.03Sm^{3+}$, $Ca_{0.70}Sr_{0.18}MoO_4$:$0.08Eu^{3+}$ and $Ca_{0.70}Sr_{0.255}MoO_4$:$0.03Sm^{3+}$ phosphors excited at different wavelengths. The emission spectrum of $Ca_{0.70}Sr_{0.255}MoO_4$:$0.03Sm^{3+}$ 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 $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions, respectively. In Fig. 4b and c, there are several strong and sharp peaks which are attributed to $^5D_0 \rightarrow {}^7F_J$ ($J = 1$, 2, 3, 4) charge transitions, indicating the existence of Eu^{3+} ions in the $Ca_{0.70}Sr_{0.18}MoO_4$:$0.08Eu^{3+}$ and $Ca_{0.70}Sr_{0.135}MoO_4$:$0.08Eu^{3+}$, $0.03Sm^{3+}$ matrices. The spectra consist of well resolved features at ~591, ~616, ~655, and ~703 nm, which can be assigned to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$, 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 $^5D_0 \rightarrow {}^7F_2$ 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 395 nm, and there is no 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 excited at 405 nm (Fig. 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 $^5D_0 \rightarrow {}^7F_J$ ($J = 1$, 2, 3, 4) transition of Eu^{3+} ions was observed.

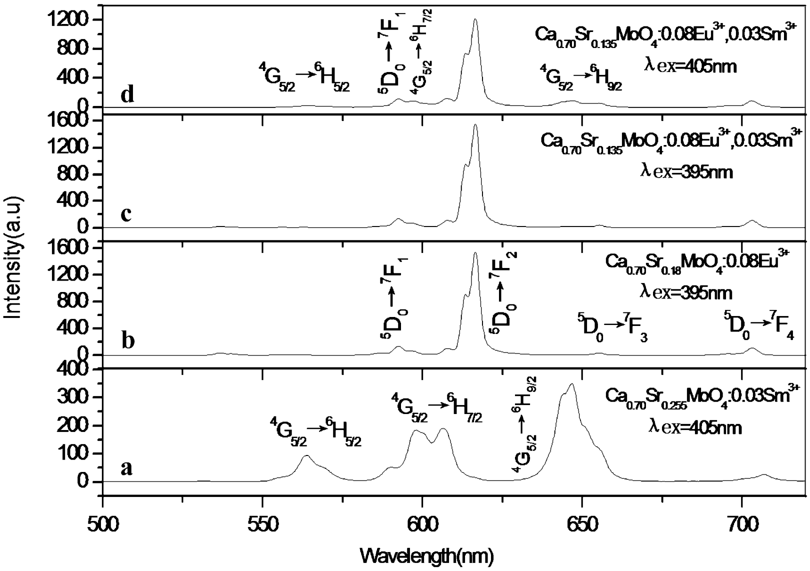

Fig. 4 The emission spectra of $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+}, $Ca_{0.70}Sr_{0.18}MoO_4$:0.08Eu^{3+} and $Ca_{0.70}Sr_{0.255}MoO_4$:0.03Sm^{3+} excited at different wavelengths

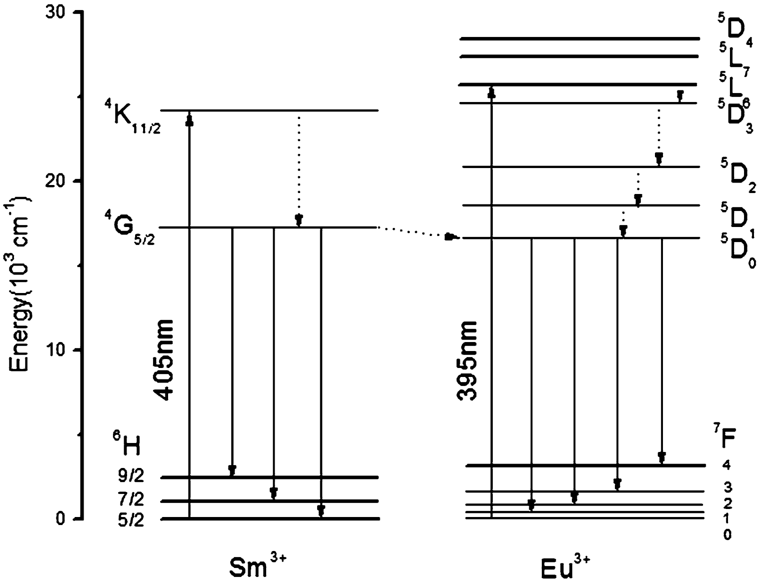

Fig. 5 Excitation, energy transfer, and emission processes of Sm^{3+} and Eu^{3+} in the $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} phosphor

A diagram of Fig. 5 shows how the rare earth ions in the $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} phosphor absorb energy (near-UV light) and emit a red light. If the $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} phosphor is excited by 395 nm corresponding to the $^7F_0 \rightarrow {}^5L_6$ of Eu^{3+}, the Eu^{3+} ion absorbs energy by itself and the energy state moves to the lowest excited energy-level ($^5D_0$) through relaxation. Finally, a red emission occurs through the $^5D_0 \rightarrow {}^7F_J$ transition. On the other hand, if the $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} phosphor is excited by 405 nm corresponding to the $^6H_{5/2} \rightarrow {}^4K_{11/2}$ of Sm^{3+}, the Sm^{3+} ion absorbs energy and the energy state moves to the lowest excited energy-level ($^4G_{5/2}$) through relaxation. The Sm^{3+} transfers this energy to the $^5D_0$ state of Eu^{3+} without any red emission. Therefore, the red emission due to Eu^{3+} occurs through the $^5D_0 \rightarrow {}^7F_J$ transition and emission due to Sm^{3+} is not observed.

4 Conclusions

In conclusion, the red-emitting phosphor $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} has been obtained successfully via 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 $^6H_{5/2} \rightarrow {}^4K_{11/2}$ 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 Sm^{3+}–Eu^{3+} co-doped $Ca_{0.70}Sr_{0.135}MoO_4$:0.08Eu^{3+}, 0.03Sm^{3+} is an excellent red-emitting phosphor for LED.

Acknowledgements The authors are grateful for the Educational Department Funds of Liaoning Province of P.R. China (Grant No. LS2010120). and the Science and Technical Projects of Shenyang (Grant No. 10633070) of People's Republic of China.

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