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Effect of surfactants on morphology and luminescent properties of $CaMoO_4$: Eu^{3+} red phosphors

Yuling Yang[a], Xueming Li[a,*], Wenlin Feng[a,b,c], Wenjin Yang[a], Wulin Li[a], Chuanyi Tao[a]

[a] College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China
[b] Department of Applied Physics, Chongqing University of Technology, Chongqing 400054, China
[c] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China

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ABSTRACT

Using polyethylene glycol (PEG), Tween-80, sodium dodecyl sulphonate (SAS) and cetyltrimethylammonium bromide (CTAB) as surfactants, $CaMoO_4$: Eu^{3+} red phosphors were prepared by co-precipitation method and their morphology, structure and luminescent properties were investigated by scanning electron microscope (SEM), X-ray diffraction (XRD) and fluorescence spectrometer. The results showed that the introduction of surfactants did not change the crystal structure of $CaMoO_4$: Eu^{3+} phosphors, but greatly influenced their morphology. $CaMoO_4$: Eu^{3+} red phosphors were prepared with 5 wt% PEG20000 having small-sized and regularly spherical morphology, and there were greater improvement in the luminescent intensity than phosphors prepared with other surfactants.

1. Introduction

$CaMoO_4$: Eu^{3+} red phosphors have many optimal performance in stability, rich 4f–4f energy level and efficient emission of electric dipole transition $^5D_0 \rightarrow {}^7F_2$, so they were considered as ideal substitution for commercial red phosphors, such as Y_2O_2S: Eu^{3+} [1,2]. $CaMoO_4$: Eu^{3+} red phosphors are commercially prepared by solid-state reaction, however, the as-prepared particles of phosphors are large-sized and irregular aggregates, which seriously affect their luminescence properties [3]. Spherical phosphors with well-crystallized micron size particles have attracted much attention for good storage density and efficient emitting [4]. However, it is still one of the most challenging issues for preparing $CaMoO_4$: Eu^{3+} red phosphors with small-sized, uniformly dispersed and spherical particles.

Compared with phosphors prepared by conventional solid-state reaction, the phosphors prepared by co-precipitation method have better morphology and stronger luminescent intensity [5,6]. However, the reaction in co-precipitation method easily forms aggregates, further influences the luminescent properties of phosphors. As we know, surfactants have electrostatic repulsion and steric hindrance. They reduce surface tension of solution, so can hinder the growth of grain and prevent the formation of aggregates, thus effectively improve the morphology and optical properties of phosphors. Chen et al. [7] reported that the variety and amount of surfactants play a key role in controlling of morphology. Yan et al. [8] reported different morphology of phosphors such as sheet, nanorods and microspheres can be obtained by hydrothermal process with different surfactants. In addition, the surfactants not only have the role of template to control the surface morphology of phosphors, but also effectively enhance the luminescent efficiency of $^5D_0 \rightarrow {}^7F_2$ [9]. So far, the effect of surfactants on morphology and luminescent properties of $CaMoO_4$: Eu^{3+} red phosphors were not yet reported.

In this work, $CaMoO_4$: Eu^{3+} red phosphors using PEG2000, PEG10000, PEG20000, Tween-80, SAS and CTAB as surfactants are prepared by co-precipitation method and the effect of surfactants on morphology of phosphors is also reported. The morphology and luminescent properties of phosphors with different amounts of PEG20000 are investigated in detail.

2. Experimental

2.1. Synthesis of $CaMoO_4$: Eu^{3+}

$CaMoO_4$: Eu^{3+} red phosphors were prepared by co-precipitation method. All starting materials were of analytical purity. First, stoichionmetric amounts of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, $Eu(NO_3)_3\cdot5H_2O$ and $Ca(NO_3)_2\cdot4H_2O$ were dissolved in distilled water under magnetic stirring and heating, then the clear solution obtained was dropped into the mixture of NH_4HCO_3-$NH_3\cdot H_2O$ precipitator with different

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* Corresponding author. Tel.: +86 23 65105659; fax: +86 23 65105659.
E-mail address: xuemingli@cqu.edu.cn (X. Li).

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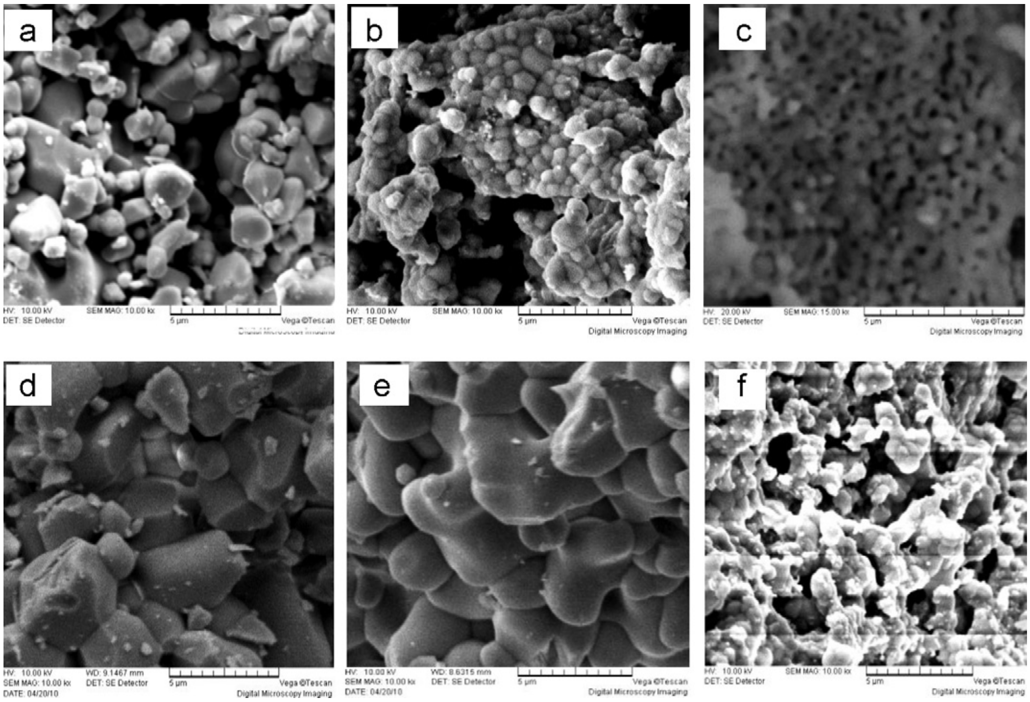

Fig. 1. Morphology of $CaMoO_4$: Eu^{3+} with different surfactants: (a) PEG2000, (b) PEG10000, (c) PEG20000, (d) Tween-80, (e) SAS, and (f) CTAB.

surfactants PEG2000, PEG10000, PEG20000, Tween-80, SAS and CTAB at a speed of 5 mL/min under continuous stirring and white precipitation generated. The white precursor was obtained after aging, filtration, washing, drying. Finally, the precursor was put into a furnace for precalcination at 500 °C for 2 h, and then calcined at 800 °C for 4 h in air, pink phosphors were obtained.

2.2. Characterization

The morphology of phosphors was performed by TESCAN VEGAIILMU scanning electron microscope. The crystal structure was characterized by X-ray diffraction with Cu Kα radiation over the 2θ rang of 10–70° with a step width of 8°/min, the accelerating voltage and emission current were 40 kV and 30 mA, respectively. The excitation and emission spectra were recorded on a RF-5301 molecular fluorescence spectrometer equipped with a xenon lamp as excitation source. All measurements were performed at room temperature.

3. Results and discussion

3.1. Effect of different surfactants on morphology of phosphors

Fig. 1 shows the SEM images of $CaMoO_4$: Eu^{3+} prepared with different surfactants by co-precipitation method. It can be seen that the morphology of phosphors changes dramatically depending on the surfactants. The size of phosphors with PEG20000 is smaller than that of phosphors with other surfactants. Nonionic surfactant PEG is not ionized in water and has good stability, which lead to a better morphology of phosphors than that of phosphors prepared with other ionic surfactant. As for PEG series, molecular weight has great influence on the morphology. The greater molecular weight, the stronger steric hindrance repulsion, the particles are accordingly more difficult to be agglomerated. Therefore, the phosphors prepared with PEG20000 exhibits smaller, uniform, and spherical particles. Although Tween-80 is also nonionic surfactant, lower molecular weight results into weak steric hindrance and further leads to irregularly large particles with hard agglomerates. The phosphors with SAS or CTAB also hardly aggregated, since the cationic surfactants easily bridge with the surface of particles and thus much large agglomerates are formed. In conclusion, the phosphors prepared with PEG20000 have better morphology than that of other phosphors. Therefore, the effect of PEG20000 on morphology, crystal structure and luminescent properties of $CaMoO_4$: Eu^{3+} red phosphors will be discussed in details.

3.2. Effect of PEG20000 amount on morphology of phosphors

The SEM images of $CaMoO_4$: Eu^{3+} phosphors prepared with different amount of PEG20000 are shown in Fig. 2. The results showed that the phosphors without surfactants are seriously aggregation with diameters of 0.2–1 μm. After adding 2.5 and 5.0 wt% PEG20000, the morphology of phosphors was notably improved, and the phosphors displayed uniform sphere-like morphology with diameters of 100 and 300 nm, respectively. The spatial compression in solution was main function when appropriate amount of surfactants was added, and the growth of particles was hindered due to the steric hindrance of PEG20000. In addition, the appropriate amount of surfactants also play role of template, which can effectively control the shape of particles [10]. Thus good dispersedly spherical particles without aggregates are formed. However, the particle sizes will increase to 400–900 nm and the phenomenon of slight agglomeration can be observed when the amount of PEG20000 increases by 10 or 15 wt%. In solution, the negative adsorption among particles appears and the depletion layer is formed on the surface of particles, and the concentration of PEG20000 on the surface of particles is lower than the concentration of PEG20000 in solution, which makes the depletion layers overlap. Thus the attractive interaction among particles increases and the nuclear grows to bigger particles with little aggregates. When the amount reaches 50 wt%, the repulsion among particles dominates in the high concentration solution of PEG20000 and the particles are in the state of depletion dispersion. Therefore, the phosphors display a non-uniform morphology with diameters of 0.5–3 μm.

3.3. Effect of PEG20000 amount on the crystal structure of $CaMoO_4$: Eu^{3+}

Fig. 3 is the XRD pattern of $CaMoO_4$: Eu^{3+} phosphors prepared with different amount of PEG20000. The pattern showed that all

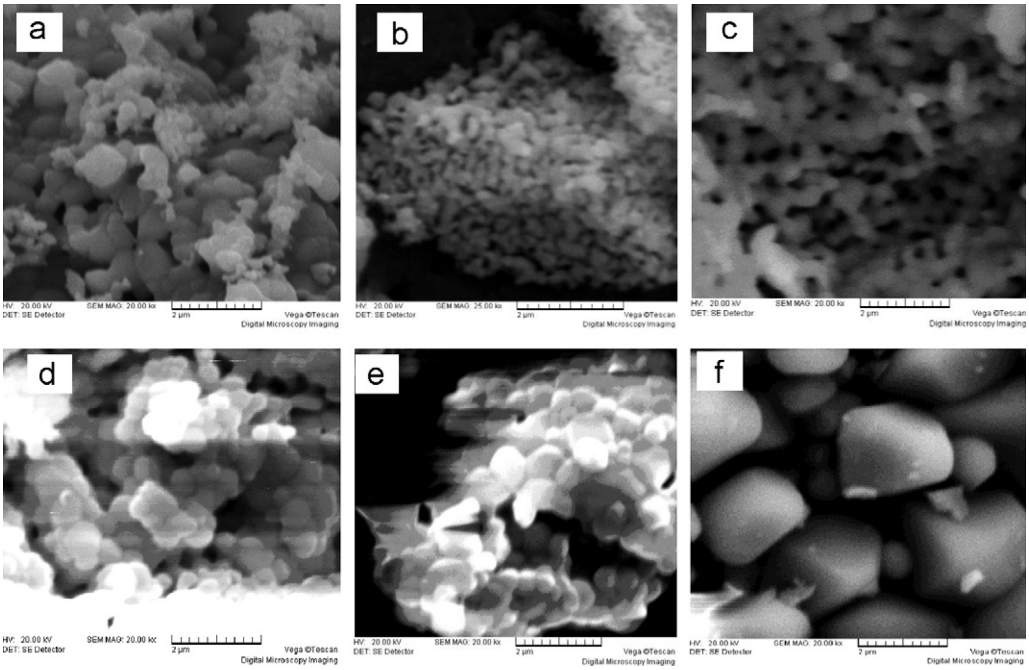

Fig. 2. Morphology of $CaMoO_4$: Eu^{3+} prepared with different amount of PEG20000: (a) 0%, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt%, (f) 50 wt%.

refection peaks corresponded to the standard file # JCPDS 29-0351 [11], which indicated the introduction of surfactants did not change the crystal structure of $CaMoO_4$: Eu^{3+} phosphors. The approximate crystallite sizes of the phosphors with different PEG20000 amount can be calculated by the Scherrer's equation [12],

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

where D is the average crystallite size, λ (=0.15405 nm) is the Cu Kα wavelength, β is the full width at half maximum (FWHM) and θ represents Bragg angle. The three XRD peaks of (1 1 2), (2 0 4) and (3 1 2) are used to calculate the mean size of the phosphors and the results are shown in Table 1. It can be seen that the average crystallite size increases with the amount of PEG20000 increases. It suggests that small amount of PEG20000 can prevent the growth of crystallite. In addition, the particles of phosphors are second aggregation of crystalline, thus the particle sizes obtained by SEM images are bigger than the calculated crystallite sizes.

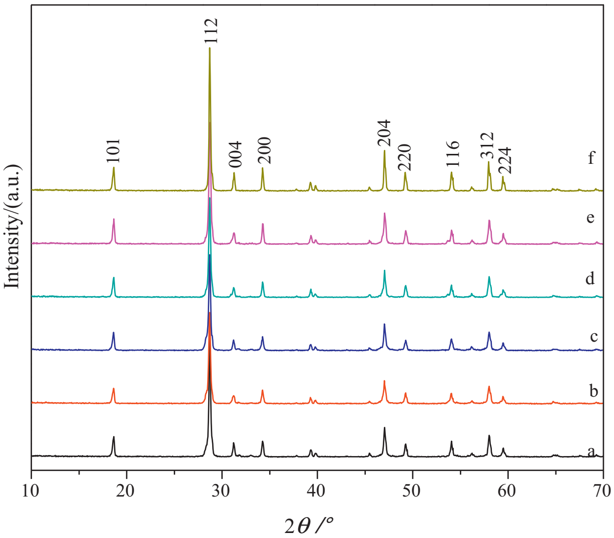

Fig. 3. XRD pattern of $CaMoO_4$: Eu^{3+} prepared with different amount of PEG20000: (a) 0%, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt%, (f) 50 wt%.

Table 1
Crystallite sizes of phosphors prepared with different PEG20000 amount.

PEG20000 amount	Crystallite sizes/nm	PEG20000 amount	Crystallite sizes/nm
0%	25.5	10 wt%	25.5
2.5 wt%	23.9	15 wt%	26.1
5.0 wt%	24.0	50 wt%	32.8

3.4. *Effect of PEG20000 amount on the luminescence properties of $CaMoO_4$: Eu^{3+}*

The excitation and emission spectra of $CaMoO_4$: Eu^{3+} were shown in Fig. 4. The broad luminescent band ranged from 290 to

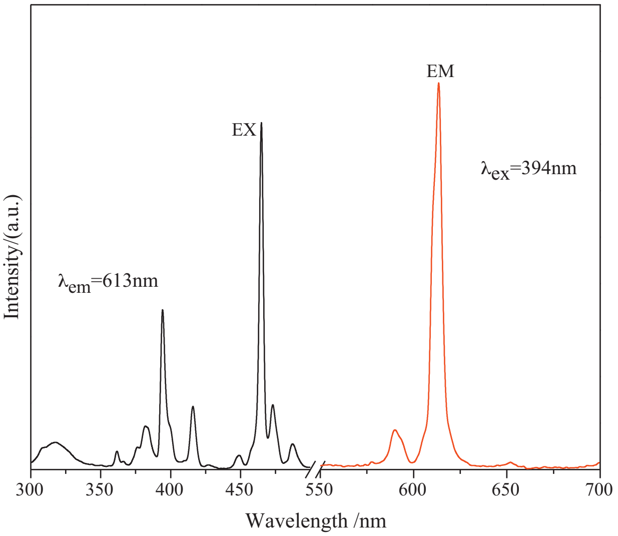

Fig. 4. Excitation and emission spectra of $CaMoO_4$: Eu^{3+} red phosphors.

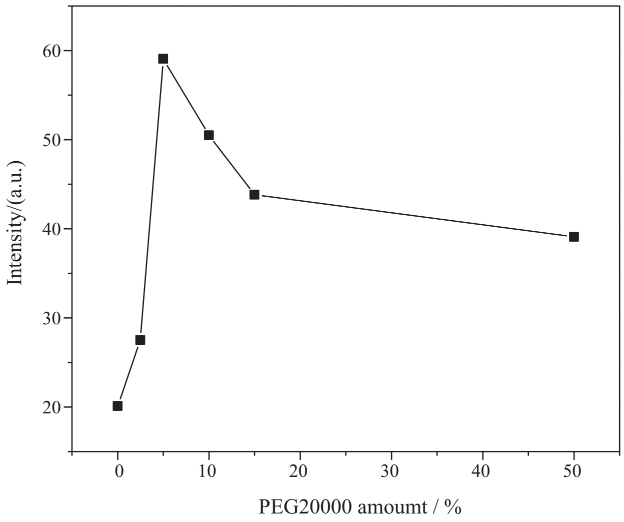

Fig. 5. Effect of PEG20000 amount on the luminescent intensity of $CaMoO_4$: Eu^{3+} red phosphors.

350 nm in the spectra is charge band of Eu–O because of the redistribution of charge density [13]. The narrow peaks ranged from 350 to 480 nm are the transitions of Eu^{3+} from the ground state to the excited state of $4f^7$ configuration, and the absorption of $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ are stronger than other peaks, which matches well with the emission wavelength of the UV-LED or the blue LED chips, and this can improve the color rendering property of commercial W-LED. In addition, the characteristic emissions of Eu^{3+}, such as $^5D_0 \rightarrow {}^7F_3$ (654 nm), $^5D_0 \rightarrow {}^7F_2$ (613 nm) and $^5D_0 \rightarrow {}^7F_1$ (590 nm), are observed and the relative intensity of $^5D_0 \rightarrow {}^7F_2$ is stronger than that of other peaks from Fig. 4. According to the spin selection rule, the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ is forbidden. However, when the 4f configuration of Eu^{3+} mixed with the opposite configurations 5d and 5g, or the symmetry deviated from the centre of inversion, the spin selection rule is relaxed and the forbidden transition of f energy levels is partially relieved, which resulted in the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ and emission of red light [14].

The luminescent properties of phosphors strongly depend on the particle size and surface morphology [8]. Fig. 5 gives the effect of PEG20000 amount on the luminescent intensity of $CaMoO_4$: Eu^{3+} red phosphors. The results showed that with the addition of different amount of surfactants, the relative intensity of peak centered at 613 nm observably enhanced and reached a maximum at 5 wt%. But when the amount of PEG20000 over 5 wt%, the intensity decreased with the increasing of the PEG20000 amount. The phosphors with 5 wt% PEG20000 are uniform, spherical particles without agglomeration, thus their luminescent properties are excellent. Although the phosphors prepared with 2.5 wt% PEG20000 are dispersed spherical particles, the particle size of phosphors has been reduced to 100 nm which has properties of quantum effects and light scattering [15], thus results in the decrease of luminescent efficiency with the decrease of particles size. When the amount of PEG20000 over 5 wt%, the agglomeration and larger particle size distribution of phosphors lead to the increasing of surface defects and decrease in exciting surface area [16]. In addition, the produced crystal nucleus are quickly encapsulated by excess PEG20000 which make the Eu^{3+} cannot completely enter into the crystal lattice of $CaMoO_4$, thus the relative intensity of phosphors is declined dramatically.

4. Conclusions

$CaMoO_4$: Eu^{3+} red phosphors were prepared by co-precipitation method with PEG2000, PEG10000, PEG20000, Tween-80, SAS and CTAB as surfactants. The phosphors prepared with PEG20000 have narrowest particle size due to the strongest steric hindrance repulsion of PEG20000. The introduction of surfactants does not change the crystal structure of $CaMoO_4$: Eu^{3+} phosphors. When the amount of PEG20000 is 5 wt%, the phosphors display uniform sphere-like morphology with diameters of 300 nm, and the strongest red luminescent intensity at 613 nm attributed to the hypersensitive electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ is obtained. In addition, their excitation spectra present strong absorption at near-UV light (394 nm) and blue light (465 nm), which match well with commercial LED chips.

In conclusion, the results showed that the surfactants played an important role in controlling the morphology of phosphors and the luminescent property is improved dramatically by using surfactants. Thus, the $CaMoO_4$: Eu^{3+} red phosphors prepared with 5 wt% PEG20000 are promising substitution for commercial red phosphors and can effectively improve the performance properties of commercial W-LED.

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