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Green synthesis of nanoparticles molybdate doped with rare earth ion and its luminescence property

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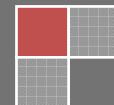
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ABSTRACT

Nanoparticles calcium molybdate doped with Eu³⁺ were synthesized by sol-gel method, which were measured by DSC, XRD, SEM and PL to character the optimum calcination temperature, the crystalline phase, morphology and luminescence properties. The influence of pH and doping amount of Eu³⁺ on these nanoparticles was also investigated. The results showed that CaMoO₄: Eu³⁺ (6%, mass ratio) prepared in pH value 7-9 and calcined at 700 °C became uniformly cubic crystal and exhibited red photoluminescence with strongest emission peak at 612nm by 258 nm excitation, which was caused by ⁵D₀→⁷F₂ transition of Eu³⁺. It can be predicted this CaMoO₄: Eu³⁺ phosphor could be a potential phosphor material for white-light LED application in the future.

KEYWORDS

Molybdate; Sol-gel method; Luminescence property; Phosphor.



INTRODUCTION

With the rapidly increasing demand of energy consumption and energy crisis, the LED white light is considered to be environmentally-friendly and energy-saving in the 21st century^[1]. The phosphor synthesized by molybdate doped rare earth ions plays an important role in the LED white light. Especially, the white light chromaticness of red phosphor combined with green or blue phosphor, which is effectively stimulated by near ultraviolet, is better than that of the traditional one^[2-4]. Therefore, the research on red phosphors doped with rare earth (Eu^{3+} , Sm^{3+} , Pr^{3+}) is becoming a hot spot^[5-8].

Recently, various synthetic routes such as solid-state reaction, hydrothermal method and microwave radiation synthesis have been used to prepare phosphor^[9,10]. However, most of these methods need high reaction temperature and large energy, while the sol-gel method can overcome these shortcomings to realize uniform dispersion at molecular level. In this paper, the red phosphor CaMoO_4 : Eu^{3+} was synthesized by sol-gel method, some synthesis conditions including sintering temperature, doping concentration and the value of pH were investigated. And its crystalline phase, morphology and luminescence properties was characterized by XRD, SEM and PL.

EXPERIMENTAL

Materials

Analytical pure compounds CaCl_2 , $\text{Eu}(\text{NO}_3)_3$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were bought from Tianjing Chemical Plant; $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, 6000-7500, from GuangDong XiLong Chemical.

Measurement

The structure of samples was characterized by X-ray powder diffraction (XRD, D8 Advance, Bruker). The excitation and emission spectra were recorded by Spectrophotometers (UV-Vis Perkin Elmer Lambda35 equipped with an integrating sphere, BaSO_4 as the reflection-background contrast; LS55 Fluorescence Spectrometer). The morphology was obtained by SEM (FEI Quanta 200 FEG, 40kV, 150mA, scan range 15° - 65° , scan rate $2^\circ/\text{min}$).

Synthesis of CaMoO_4 by sol-gel method

Defined calculated amount of CaCl_2 and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ together with polyethylene glycol (PEG) were dissolved in deionized water, stirred for 30 min at 40°C to form white gel, then heated to obtain the samples at 500°C , 600°C , 700°C , 800°C and 900°C , respectively.

Synthesis of CaMoO_4 : Eu^{3+} by sol-gel method

Calculated amount of $\text{Eu}(\text{NO}_3)_3$ were added into the above solutions. The latter process was the same as the previous to obtain different concentration of CaMoO_4 : Eu^{3+} samples.

RESULTS AND DISCUSSION

Thermal analysis and XRD of samples

As shown in Figure 1a, the small weight loss of 0.93 % from room temperature to 130°C is probably due to the elimination of the absorbed water corresponding to a wide endothermic peak in the DSC curve at 51°C . From 130°C to 900°C , there is a strong endothermic peak at 529°C and has a 4.0 % weight loss. This can be associated with the loss of bonding water, which is formed by hydrone and the component of CaMoO_4 , and residual hydroxyl. When the reaction system is added PEG (Figure 1b), the weight loss of 1.1 % from room temperature to 122°C is also attributed to the elimination of the absorbed water, corresponding to a wide endothermic peak in the DSC curve at 44°C . As present in the figure, there are two small endothermic peaks at 523°C and 648°C , and the weight loss is about 4.3%. These results suggest that CaMoO_4 is basically stable at 500°C , so we select the temperature of 500°C , 600°C , 700°C , 800°C and 900°C to calcine.

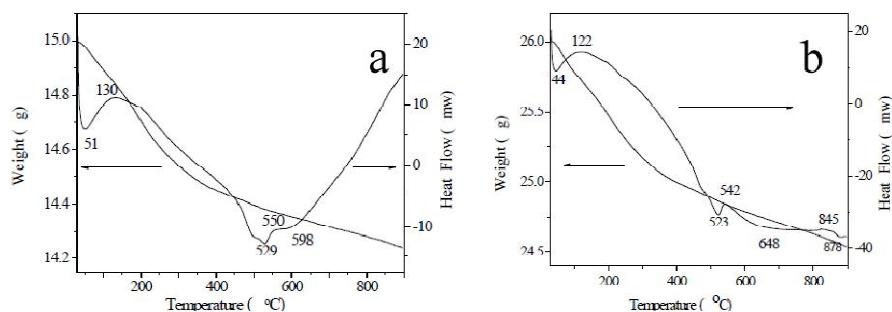


Figure 1: TG-DSC curve of CaMoO₄ (a, no addition PEG; b, addition PEG)

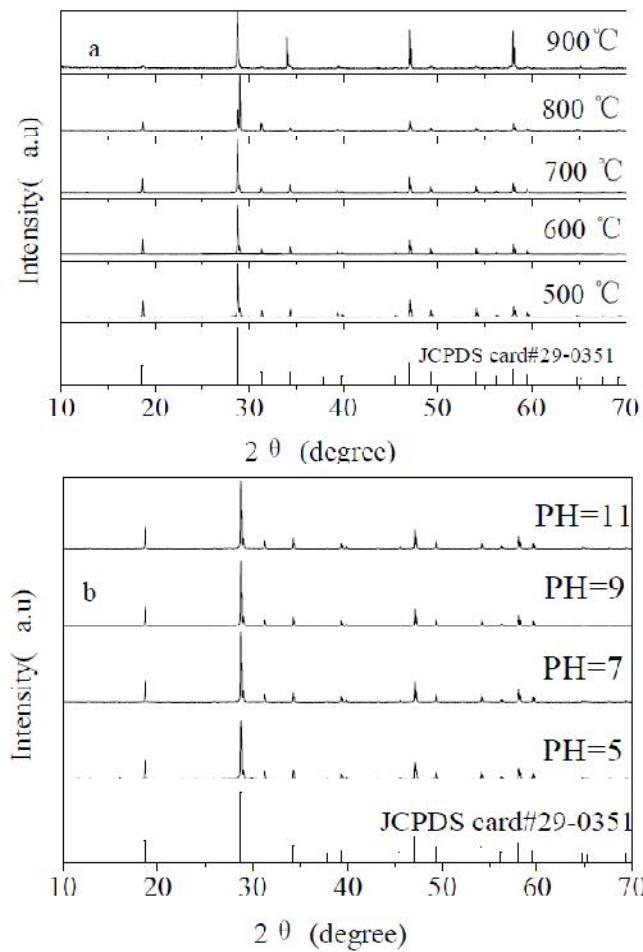


Figure 2: XRD patterns of the CaMoO₄ samples (addition PEG) obtained at different firing temperature (2a) and different PH value (2b)

Figure 2a shows the XRD patterns of as-prepared samples. The position and intensity of diffraction peaks are basically unanimous at 500 °C, 600 °C and 700 °C, indicating that the phase is stable at this temperature range. When the temperature is 800 °C, the position and intensity of diffraction peaks of the sample are the same as that of 500-700 °C. However, the peaks of the sample become to change at 800 °C, which indicates that it might be a new phase. The diffraction peaks at 900 °C are different from the peaks at 500-700 °C. It can be speculated that it is a new phase or another substance. The appropriate temperature of synthesis CaMoO₄ is in the range of 500-700 °C. According to Figure 2b, when the PH value of solution ranges from 7 to 11, products will quickly generate. The XRD patterns of the products are successively consistent with the standard map when PH value between 7-9.

Photoluminescence properties of samples

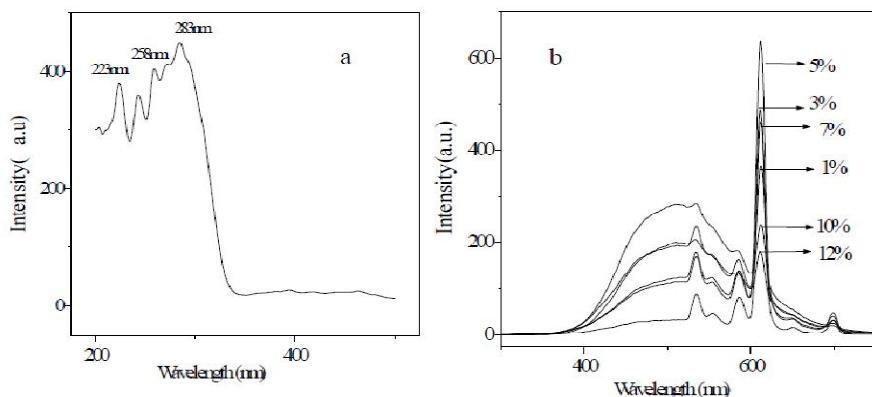


Figure 3: Excitation spectrum of $\text{CaMoO}_4 : \text{Eu}^{3+}$ with different amount of Eu^{3+} doping under 258nm excitation

The $\text{CaMoO}_4 : \text{Eu}^{3+}$ red phosphor can be stimulated at 223 nm, 258 nm and 283 nm, which are the same as the wavelength of LED chip (Figure 3a). So this phosphor can be used as red phosphor of LED white light. The main peak at 612 nm corresponds to ${}^5\text{D}_0 - {}^7\text{F}_2$ electric dipole transition of Eu^{3+} .

The intensity of light is different accompanied by the different amount of doping Eu^{3+} under the excitation of 258 nm (Figure 3b). When the doping content is from 2% to 6%, the intensity is becoming stronger as increasing content, while it is strongest at 6% Eu^{3+} . But the intensity becomes weaker while the content is more than 6% because of the concentration quenching phenomenon.

Morphology characterization of samples

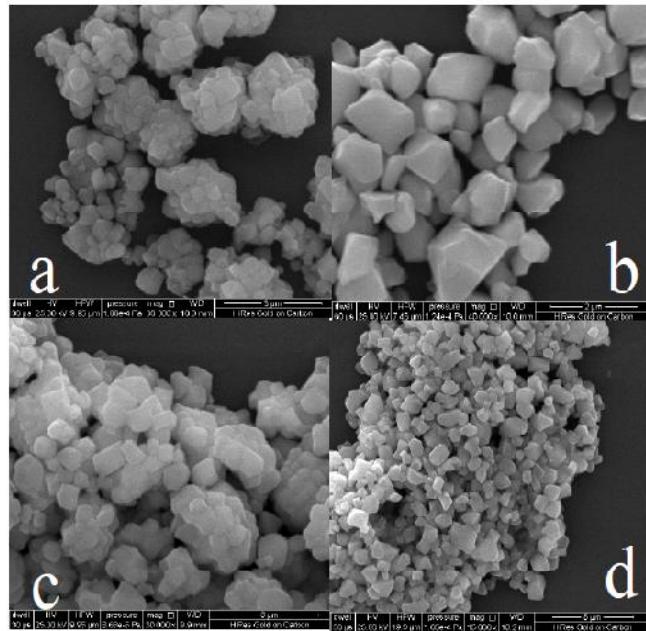


Figure 4: SEM images of CaMoO_4 . 4a,4b fired at 500 °C and 700 °C respectively (no addition PEG), 4c,4d CaMoO_4 and $\text{CaMoO}_4 : \text{Eu}^{3+}(5\%)$ fired at 700 °C (addition PEG)

In Figure 4a, the SEM image of CaMoO_4 prepared at 500 °C with no PEG in the synthesis process shows a number of agglomerated particles and the size of particles is basically uniform. When CaMoO_4 prepared at 700 °C, these particles are rarely agglomerated and the size is also uniform (Figure 4b). However, when PEG is in added in the prepared process, the particles become agglomerated (Figure 4c). In Figure 4d the $\text{CaMoO}_4 : \text{Eu}^{3+}(5\%)$ prepared at 700 °C with PEG in the synthesis process shows uniformly cubic crystal.

CONCLUSIONS

In this study, we prepared CaMoO₄: Eu³⁺ red phosphors by sol-gel method, which was characterize by TG-DSC, XRD, SEM and PL spectra. The thermal analysis and the XRD results indicates that the powder calcined at 700 °C can be obtained pure phase and the phase might change at higher temperature. The CaMoO₄: Eu³⁺ can be emitted red light at 223 nm, 258 nm and 283 nm by ultraviolet light, and the maximum emission peak is 612 nm, which coincide with the emitting light of near ultraviolet and blue LED chips. When 6% Eu³⁺ is added, the intensity of light becomes strongest among the reported content.

ACKNOWLEDGEMENT

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