



Synthesis and Luminescence Property of Red Phosphor $\text{CaMoO}_4:\text{Eu}^{3+}$ via Sol-Gel Method

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Red phosphors played an important role on optimizing the LED white light chromaticness. $\text{CaMoO}_4:\text{Eu}^{3+}$ was synthesized by sol-gel method, which was characterized by X-ray powder diffraction, scanning electron microscope and photoluminescence spectra. The results showed that $\text{CaMoO}_4:\text{Eu}^{3+}$ (5 %, mass ratio) prepared in pH value of 7-11 and calcined at 700 °C became uniformly cubic crystal and exhibited red photoluminescence with strongest emission peak at 612 nm by 258 nm excitation, which was caused by ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} .

Keywords: Molybdate, Sol-gel method, Red phosphor.

INTRODUCTION

The LED white light is considered to be one of the environmentally-friendly and energy-saving sources in the 21st century¹. The phosphors that were synthesized by molybdate salt with doping 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^{2,3}. Therefore, the research on red phosphors doped with rare earth (Eu^{3+} , Sm^{3+} , Pr^{3+}) is becoming a hot spot⁴⁻⁸.

Recently, various synthetic routes such as solid-state reaction, sol-gel process, hydrothermal method and microwave radiation synthesis⁹, have been used to prepare phosphor. The research of molybdate matrix is mainly concentrated on red phosphor prepared by solid-state method^{10,11}. However, this method needs high reaction temperature and large energy, thus the reaction speed is relatively fast resulting in nonuniform size of product. The sol-gel method can overcome these shortcomings to realize uniform dispersion at molecular level. In this paper, the red phosphor $\text{CaMoO}_4:\text{Eu}^{3+}$ was synthesized by sol-gel method. Some synthesis conditions including sintering temperature, doping concentration and the value of pH were also investigated. Its crystalline phase, morphology and luminescence properties were characterized by XRD (D8 Advance, Bruker), SEM (Quanta 200, FEI) and photoluminescence (Perkin Elmer, USA).

EXPERIMENTAL

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 0.5 min at 40 °C to form white gel, then heated at 500, 600, 700, 800 and 900 °C, respectively to obtain the samples.

Synthesis of $\text{CaMoO}_4:\text{Eu}^{3+}$ 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 $\text{CaMoO}_4:\text{Eu}^{3+}$ samples.

RESULTS AND DISCUSSION

As shown in Fig. 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. There is a strong endothermic peak at 529 °C and a 4 % 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 (Fig. 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 shown in the figure, there are two small endothermic peaks at 523 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, 600, 700, 800 and 900 °C to calcine.

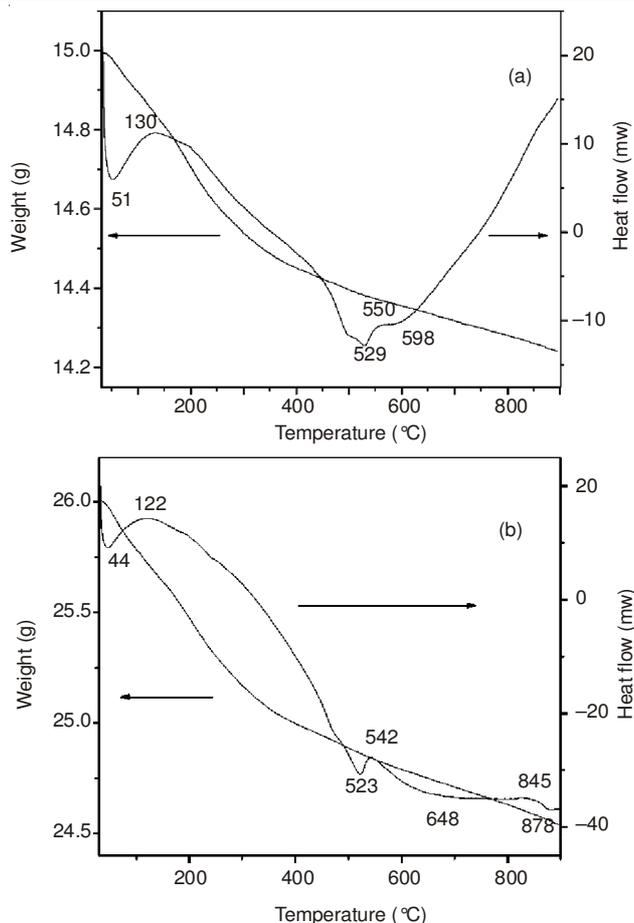


Fig. 1. TG-DSC curve of CaMoO_4 (a) no addition PEG; (b) addition PEG

Fig. 2a shows the XRD patterns of as-prepared samples. The position and intensity of diffraction peaks are basically unanimous at 500, 600 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 CaMoO_4 ranges from 500 to 700 °C. According to Fig. 2b, when the pH value of solution reaches from 7 to 11, products will quickly generate. The XRD patterns of the products are consistent with the standard map.

The $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphor can be stimulated at 223, 258 and 283 nm, which are the same as the wavelength of LED chip (Fig. 3). So this phosphor can be used as red phosphor of LED white light. The main peak at 612 nm corresponds to $^5\text{D}_0\text{-}^7\text{F}_2$ 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. When the doping content is from 1 to 5 %, the intensity is becoming stronger as increasing content, while it is strongest at 5 % Eu^{3+} . But the intensity becomes weaker while the content is more than 5 % because of the concentration quenching phenomenon.

In Fig. 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.

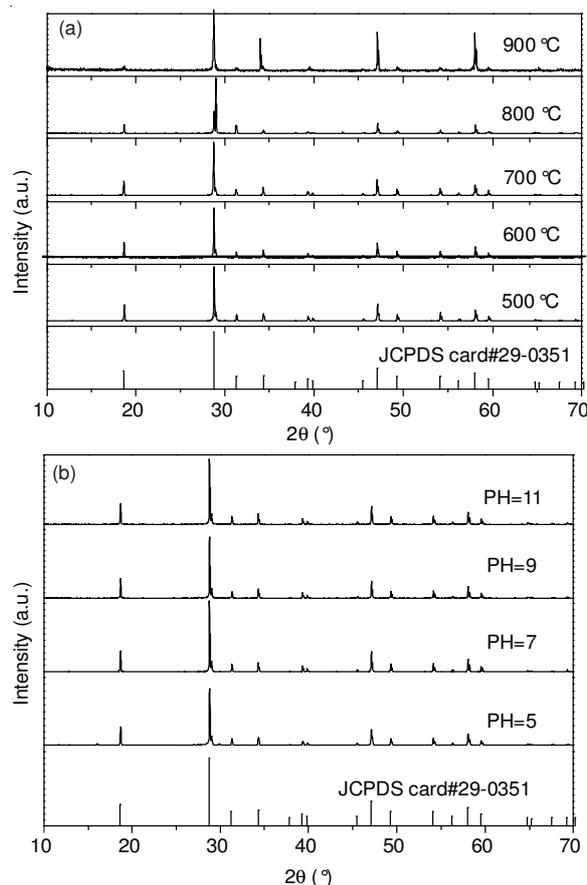


Fig. 2. XRD patterns of the CaMoO_4 samples (addition PEG) obtained at different firing temperature (a) and different pH value (b)

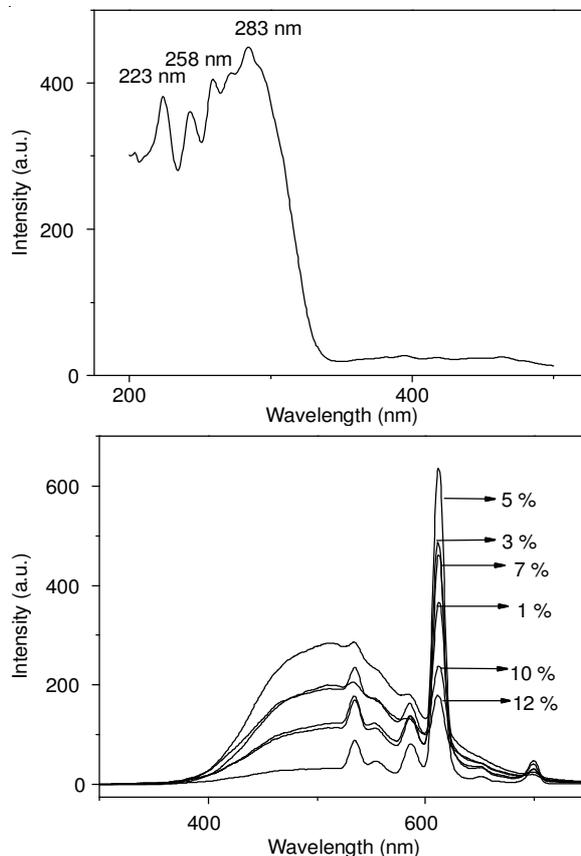


Fig. 3. Excitation spectrum of $\text{CaMoO}_4:\text{Eu}^{3+}$ with different amount of Eu^{3+} doping under 258 nm excitation

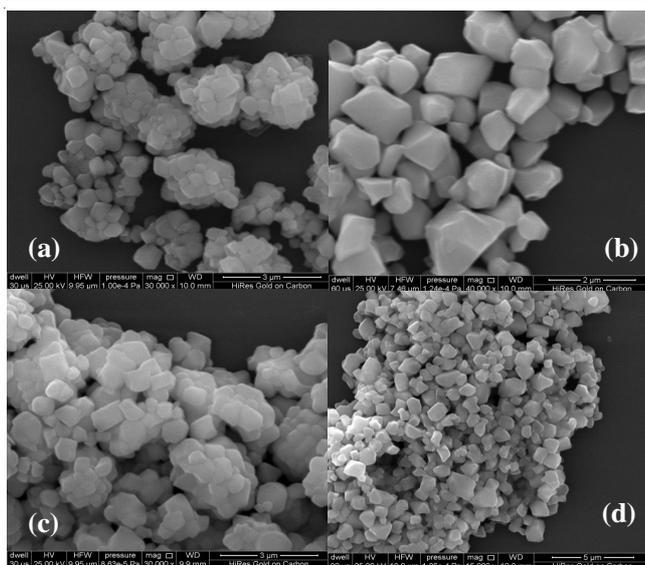


Fig. 4. SEM images of CaMoO_4 ; (a, b) fired at 500 and 700 °C, respectively (no addition PEG), (c, d) CaMoO_4 and $\text{CaMoO}_4:\text{Eu}^{3+}$ (5 %) fired at 700 °C (addition PEG)

When CaMoO_4 prepared at 700 °C, these particles are rarely agglomerated and the size is also uniform (Fig. 4b). However, when PEG is added in the prepared process, the particles become agglomerated (Fig. 4c). In Fig. 4d the $\text{CaMoO}_4:\text{Eu}^{3+}$ (5 %) prepared at 700 °C with PEG in the synthesis process shows uniformly cubic crystal.

Conclusion

In this study, we prepared $\text{CaMoO}_4:\text{Eu}^{3+}$ red phosphors by sol-gel method, which was characterized by TG-DSC, XRD, SEM and photoluminescence spectra. The thermal analysis shows that the absorbed water of CaMoO_4 is basically stripped at 500 °C. The XRD results indicate that the powder calcined

500-700 °C can be obtained CaMoO_4 pure phase and the phase might change at higher temperature. The $\text{CaMoO}_4:\text{Eu}^{3+}$ can be emitted red light at 223, 258 and 283 nm by ultraviolet light and the maximum emission peak is 612 nm, which coincides with the emitting light of near ultraviolet and blue LED chips. When 5 % Eu^{3+} is added, the intensity of light becomes strongest among the content of 1, 3, 5, 7, 10 and 12 %.

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REFERENCES

1. W.J. Yang, L.Y. Luo, T.-M. Chen and N.-S. Wang, *Chem. Mater.*, **17**, 3883 (2005).
2. T.R.N. Kutty and A. Nag, *J. Mater. Chem.*, **13**, 2271 (2003).
3. Z. Wang, X. Zhang, J. Chang and C. Li, *J. Rare Earths*, **29**, 1018 (2011).
4. J.-Z. Chang, M. Li and H.-Z. Shi, *J. Inorg. Mater.*, **21**, 565 (2006).
5. Y. Wei, F.Q. Lu, X.R. Zhang and D.P. Chen, *Mater. Lett.*, **61**, 1337 (2007).
6. J.Q. Wang, J. Yang, Y.L. Jin and T. Qiu, *J. Rare Earth*, **29**, 562 (2011).
7. Z. Zhicheng, Z. Yongping, L. Fachun, L. Heng, H. Zhinan and H. Zhigao, *J. Rare Earths*, **24**, 270 (2006).
8. H.X. Mai, Y.W. Zhang, R. Si, Z.G. Yan, L.- Sun, L.-P. You and C.-H. Yan, *J. Am. Chem. Soc.*, **128**, 6426 (2006).
9. Z. Wang, H. Liang, M. Gong and Q. Su, *Mater. Lett.*, **62**, 619 (2008).
10. C.X. Li, Z.W. Quan, P.P. Yang, J. Yang, H.Z. Lian and J. Lin, *J. Mater. Chem.*, **18**, 1353 (2008).
11. Y.Sh. Hu, W.D. Zhuang, H.Q. Ye, D. Wang, S. Zhang and X. Huang, *J. Alloys Comp.*, **390**, 226 (2005).