Advance Journal of Food Science and Technology 9(7): 519-522, 2015
DOI: 10.19026/ajfst.9.1958
ISSN: 2042-4868; e-ISSN: 2042-4876

Submitted: March 9, 2015 Accepted: April 1, 2015 Published: September 05, 2015

Research Article

Green Synthesis of Nanoparticles Molybdate Doped with Rare Earth Ion and Its Luminescence Property

Wang Jun, Feng Cai-Ting and Yu Hai-Hui
Department of Chemistry, Zhoukou Normal University, Zhoukou 466001, Henan, P.R. China

Abstract: The aim of this study is to prepare nanoparticles molybdates doped with rare earth ion Eu^{3+} synthesized by sol-gel method to study the luminescence property of these crystal powders. The influence of pH and doping amount of Eu^{3+} on these nanoparticles was also investigated. The results showed that $CaMoO_4$: Eu^{3+} (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 612×258 nm excitation, which was caused by $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. It can be predicted this $CaMoO_4$: Eu^{3+} phosphor could be a potential phosphor material for white-light LED application in the future.

Keywords: Luminescence property, molybdate, phosphor, sol-gel method

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. The phosphor synthesized by molybdate doped rare earth ions plays an important role in the LED white light (Xu *et al*., 2007). 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 (Wei *et al*., 2006). Therefore, the research on red phosphors doped with rare earth (Eu^{3+}, Sm^{3+}, Pr^{3+}) is becoming a hot spot (Wang *et al*., 2006).

Recently, various synthetic routes such as solid-state reaction, hydrothermal method and microwave radiation synthesis have been used to prepare phospho (Shi *et al*., 2012; Liu *et al*., 2007). As we know, most of these methods need high reaction temperature and large energy, but the sol-gel method can overcome these shortcomings to realize uniform dispersion at molecular level (Li, 2010). Thus, sol-gel method was utilized to synthesize the red phosphor $CaMoO_4$: Eu^{3+} in this study and its crystalline phase, morphology and luminescence properties was characterized by XRD, SEM and PL.

MATERIALS AND METHODS

Materials: Analytical pure compounds $CaCl_2$, Eu $(NO_3)_3$ and Na_2MoO_4•$2H_2O$ were bought from Tianjing Chemical Plant; HO (CH_2CH_2O) nH, 6000-7500, from GuangDong XiLong Chemical.

Measurements: 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 Lambda 35 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, 40 kV, 150 mA, scan range 15°-65°, scan rate 2°/min).

Synthesis of $CaMoO_4$ by sol-gel method: Defined calculated amount of $CaCl_2$ and $Na_2MoO_4 \cdot 2H_2O$ 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 sampls at 500, 600, 700, 800 and 900°C, respectively.

Synthesis of $CaMoO_4$: Eu^{3+} by sol-gel method: Calculated amount of Eu $(NO_3)_3$ 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 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. From 130 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

Corresponding Author: Wang Jun, Department of Chemistry, Zhoukou Normal University, Zhoukou 466001, Henan, P.R. China

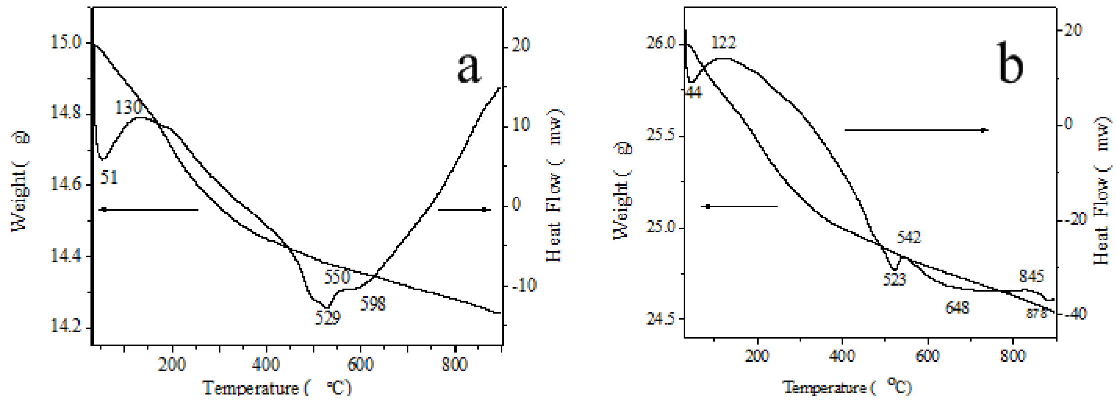
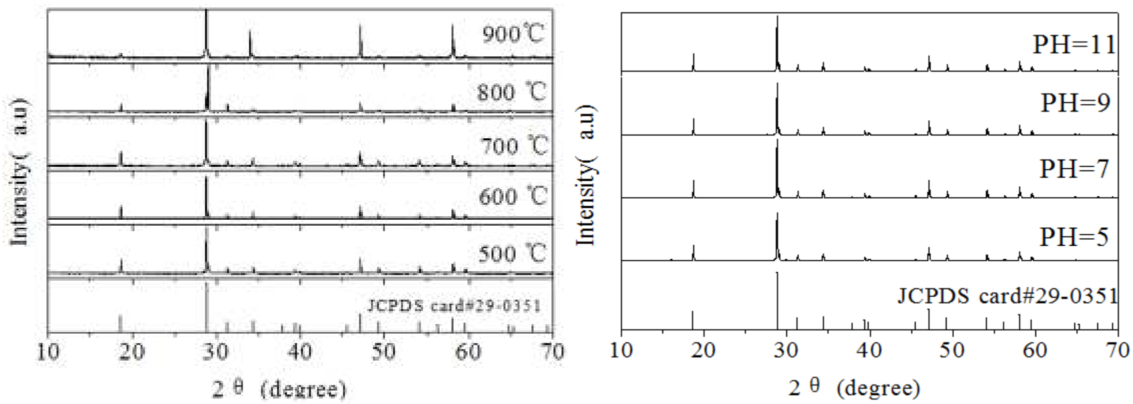


Fig. 1: TG-DSC curve of $CaMoO_4$; (a): No addition PEG; (b): Addition PEG



(a) (b)

Fig. 2: XRD patterns of the $CaMoO_4$ samples (addition PEG) obtained at; (a): Different firing temperature; (b): Different PH value

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 present 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, respectively to calcine.

Figure 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, respectively 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 $CaMoO_4$ is in the range of 500-700°C. According to Fig. 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: The $CaMoO_4$: Eu^{3+} red phosphor can be stimulated at 223, 258 and 283 nm, respectively which are the same as the wavelength of LED chip (Fig. 3a). So this phosphor can be used as red phosphor of LED white light. The main peak at 612 nm corresponds to $^5D_0$-$^7F_2$ 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 (Fig. 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.

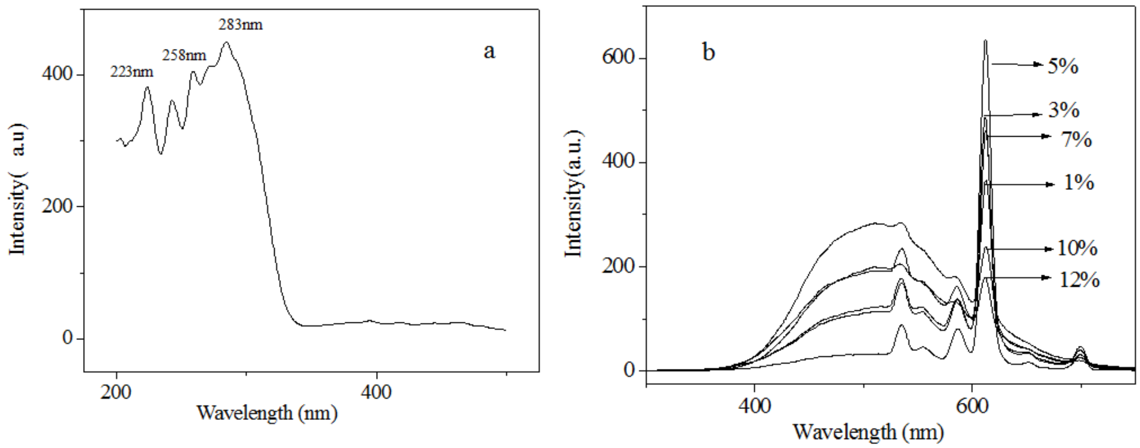


Fig. 3: Excitation spectrum of $CaMoO_4$: Eu^{3+} with different amount of Eu^{3+} doping under 258 nm excitation

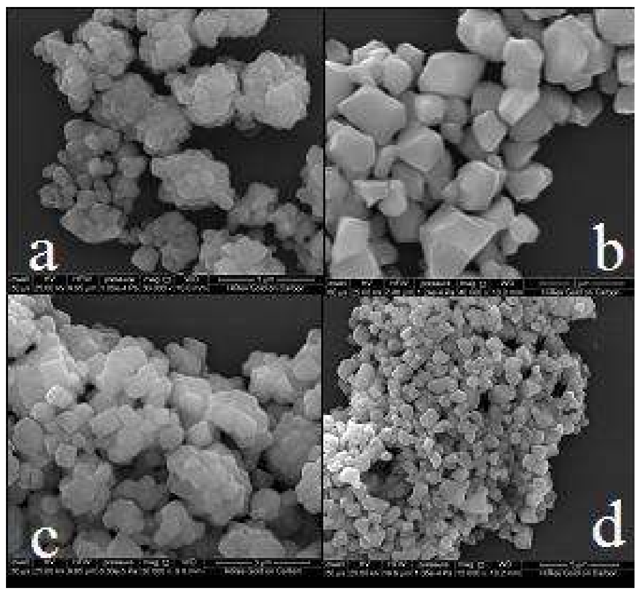


Fig. 4: SEM images of $CaMoO_4$; (a, b): Fired at 500 and 700°C, respectively (no addition PEG); (c, d): $CaMoO_4$ and $CaMoO_4$: Eu^{3+} (5%) fired at 700°C (addition PEG)

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

CONCLUSION

In this study, we prepared $CaMoO_4$: Eu^{3+} 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 $CaMoO_4$: Eu^{3+} can be emitted red light at 223, 258 and 283 nm, respectively 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% Eu^{3+} is added, the intensity of light becomes strongest among the reported content.

ACKNOWLEDGMENT

This study is supported by the Program for Science and Technology Research Projects of Henan Province (No. 142300410353).

REFERENCES

Li, H.B., 2010. Study on luminescent properties of the red phosphor NaEu $(MoO_4)_2$ prepared via sol-gel process [J]. Liaoning Chem. Ind., 39(10): 1010-1013.

Liu, J., H.Z. Lian and C.S. Shi, 2007. Improved optical photoluminescence by charge compensation in the phosphor system CaMoO4: Eu^{3+} [J]. Opt. Mater., 29(12): 1591-1594.

Shi, W.J., X.L. Zhang, C.Y. Li *et al*., 2012. Synthesis and luminescent properties of $NaAlSiO_4$:Eu^{3+} phosphors using coal fly ash as starting materials [J]. J. Chinese Rare Earth Soc., 30(3): 315-319.

Wang, X., J. Zhuang, Q. Peng and Y.D. Li, 2006. Hydrothermal synthesis of rare-earth fluoride nanocrysals. [J]. Inorg. Chem., 45(17): 6661-6667.

Wei, X.W., J. Xu, X.J. Song, Y.H. Ni, P. Zhang, C.J. Xia, G.C. Zhao and Z.S. Yang, 2006. Multi-walled carbon nanotubes coated with rare earth fluoride $EuFB_3B$ and $TbFB_3B$ nanoparticles [J]. Mater. Res. Bull., 41: 92-99.

Xu, X.D., G.Z. Xu, Z.C. Wu *et al*., 2007. Research progress on phosphors for white light-emitting diodes [J]. Acta Sci. Naturalium Univ., Sunyatseni, 46(5): 124-128.