

Sol-Gel Synthesis and Luminescence Properties of ZnMoO₄:Tb³⁺ Nano-Structural Materials

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The ultraviolet excitation molybdates-based green phosphors were synthesized by sol-gel method and characterized by X-ray powder diffraction, photoluminescence spectrum, UV-visible absorption spectrum and scanning electron microscopy. A systematic study about the effects of calcinations temperature on the composition and luminescent properties of the phosphors has also been undertaken. The result of XRD reveals that the ZnMoO₄: Tb³⁺ phosphors have triclinic structure of bulk ZnMoO₄. Under the excitation of 275 nm, the emission intensity of the self-activation phosphor MoO₄²⁻ is weakened greatly, while that of Tb³⁺ ⁵D₄→⁷F₅ transition at 543 nm (green light) is significantly enhanced. These observed luminescent properties of this phosphor demonstrate it has potential applications as luminescent material in lighting, display, *etc.*

Key Words: Sol-gel Method, ZnMoO₄, Rare earth ion, Photoluminescence.

INTRODUCTION

Recently, the exploration of novel materials and energies attracts much attention in P.R. China, especially molybdates- or tungstates-based phosphors with Eu³⁺ doped have been investigated^{1,2} due to their high stability and high emission efficiency. However, most of the studies focused on red phosphors, rarely on other colour³. It's known that molybdates intrinsically show blue-green fluorescence under the excitation by UV light and Tb³⁺ emits green light. Therefore, we can get green phosphors *via* doping appropriate amounts of Tb³⁺ to molybdates or tungstates⁴⁻⁷.

Molybdates- or tungstates-based phosphors mostly prepared by the conventional solid-state reaction. The size distribution of particles obtained by this method is irregular and this method is also high power consumption, these disadvantages can be overcome by sol-gel method which having the advantages of benign reaction conditions and good homogeneity *etc.*

ZnMoO₄ phosphors are triclinic structure and self-luminescence fluorescence chromophores, can easily forming complex ion luminescence center with closed shell electron configuration. MoO₄²⁻ has tetrahedral structure, showing green emission under the excitation by UV light (250-310 nm)^{8,9}. Herein, we present a novel green phosphor, ZnMoO₄ doping Tb³⁺ prepared by sol-gel method. Under the excitation of 275 nm, the emission intensity of the activation self-luminescent MoO₄²⁻ is weakened greatly, while that of Tb³⁺ ⁵D₄→⁷F₅ transition at 543 nm (green emission) is significantly enhanced.

EXPERIMENTAL

0.1 mol L⁻¹ Tb(NO₃)₃ solution, Na₂MoO₄·2H₂O, analytical pure, bought from Beijing Chemical Plant; ZnCl₂, analytical pure, bought from Xi'an Chemical Reagent Factory; HO(CH₂CH₂O)_nH, 6000-7500, GuangDong XiLong Chemical.

Measurement: X-ray diffraction (D₈ Advance, Bruker); scanning electron microscope (Quanta 200, FEI); UV-VIS spectroscopy (Perkin Elmer, USA); LS55 Luminescence spectrometer (Perkin Elmer, USA).

Firstly, 2.4228 g Na₂MoO₄·2H₂O and 1.3629 g ZnCl₂ were dissolved in deionized water under continuous stirring at room temperature until forming homogeneous solution. The transparent gel was formed after stirred at 80 °C for half an hour and filtrated. Secondly, the gel was transferred into a surface plate and maintained at 140 °C in drying oven for 2 h to form white gel and then divided into three parts. Finally, the samples were obtained after placing in Muffle furnace at 500 °C, 700 °C, 900 °C calcined for 4 h, respectively.

Firstly, 1 mL, 3 mL, 5 mL, 7 mL of 0.1 mol L⁻¹ Tb(NO₃)₃ were added to beakers which contain four equal parts of 2.4512 g Na₂MoO₄·2H₂O, 1.9370 g ZnCl₂ and 0.4413 g polyethylene glycol respectively and then add 20 mL deionized water. The transparent gel was formed after stirred at 80 °C for 0.5 h and filtrated. Secondly, the gel was transferred onto a surface plate and maintained at 140 °C in drying oven for 2 h to form a white gel. Finally, the samples were obtained after placing in Muffle furnace at 900 °C calcined for 4 h.

The structure of samples was characterized by X-ray powder diffraction (XRD, D₈ Advance, Bruker). The morphology of nanoparticle was obtained by SEM (Quanta 200, FEI). UV-visible diffuse reflectance spectrum was measured on a UV-visible spectrophotometers (UV-VIS Perkin Elmer Lambda35 equipped with an integrating sphere, BaSO₄ was used for the reflection-background contrast). The excitation and emission spectra were recorded using an FLS920P Edinburgh Analytical Instrument apparatus equipped with a 450 W Xenon lamp as the excitation source.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of ZnMoO₄ prepared by sol-gel method with different calcining temperature (500 °C, 700 °C, 900 °C) for 4 h. As shown in Fig. 1, the sample still has amorphous structure under the 500 °C and the structure of crystal is not very good, yet the single crystalline phase of triclinic structure has been formed and the XRD patterns are consistent with that given in JCPDS No. 35-0765. When the temperature rises to 700 °C, the ZnMoO₄ sample was obtained completely with mixed phase appearing. With the increasing of the calcining temperature, the relative intensity of diffraction peak is increased while the width reduced, which shows that the single crystalline phase of ZnMoO₄ sample is becoming well; meanwhile, the sample has stable structure and composition at above 700 °C and ZnMoO₄ is the host which has the strongest diffraction at $2\theta = 30.054^\circ$ and the disappearance of part diffraction peak due to the high temperature destroying the phase partly.

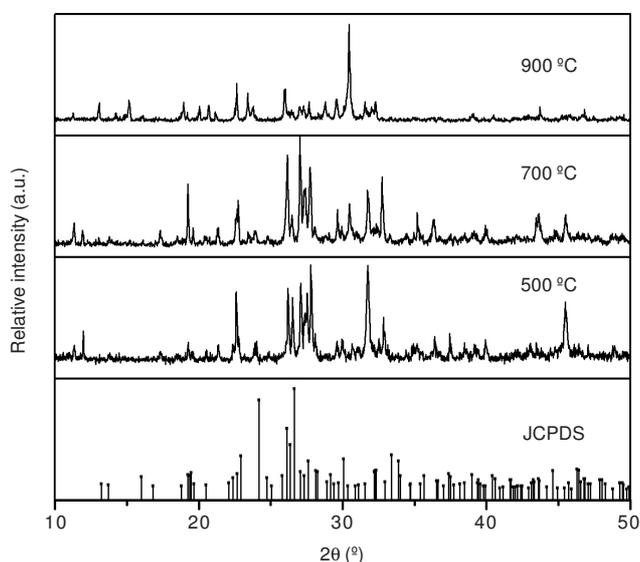


Fig. 1. XRD patterns of the samples obtained at different calcining temperature

Fig. 2 is X-ray diffraction patterns of the precursor without and with Tb³⁺ doping calcined at 900 °C for 4 h. It is obviously that the relative intensity of diffraction peak increased and the width reduced with Tb³⁺ doping and the crystalline is approximately consistent with standard spectra. Moreover, the appearance of the strongest diffraction at $2\theta = 26.633^\circ$ and the crystallographic plane at (-220), $d = 0.3344$ nm.

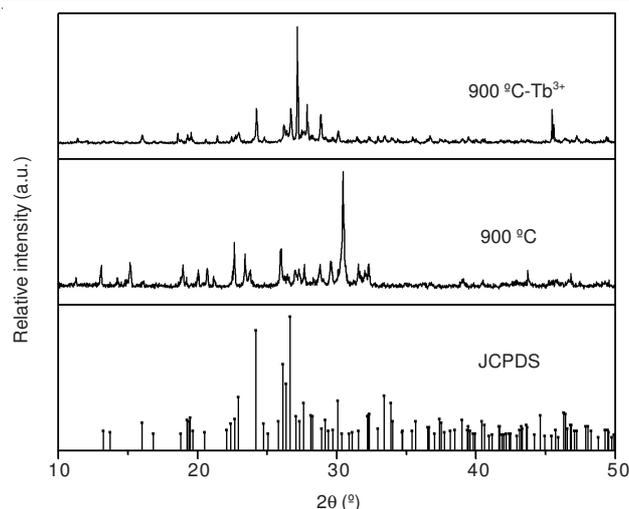


Fig. 2. XRD patterns of the samples without and with Tb³⁺ doping

The SEM images of ZnMoO₄ prepared by the sol-gel method under different calcining temperatures are shown in Fig. 3. The sample which calcined at 500 °C has granular and less rod-like shape owing to lower temperature reducing the crystallization. With the increasing of calcining temperature, in Fig. 3(b), the rod-like shape material is increased and the surface of the rods have become relatively more smooth with the appearance of irregular crystals. It is observed that regular small cubic crystals are formed in Fig. 3 (c) with 2.210 μm rod-like material appearing, which indicates that the crystallization of the sample is completed. In Fig. 3 (d), more uniform cubic crystal can be observed, with apart of defects on the surface owing to the high temperature destroying the structure partly.

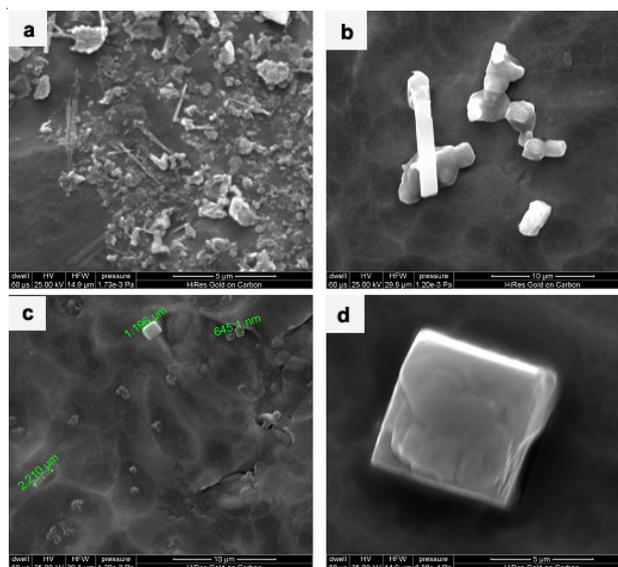


Fig. 3. SEM image of ZnMoO₄ fired at 500 °C (a), 700 °C (b, c), 900 °C (d) for 4 h

Fig. 4 demonstrates the ZnMoO₄ has strong absorption at 275 nm no matter whether it calcined at 900 °C for 4 h with Tb³⁺ doping or not, the intensity of undoped sample is stronger. Therefore, we can study their luminescent properties *via* the emission spectrum of sample excited by 275 nm.

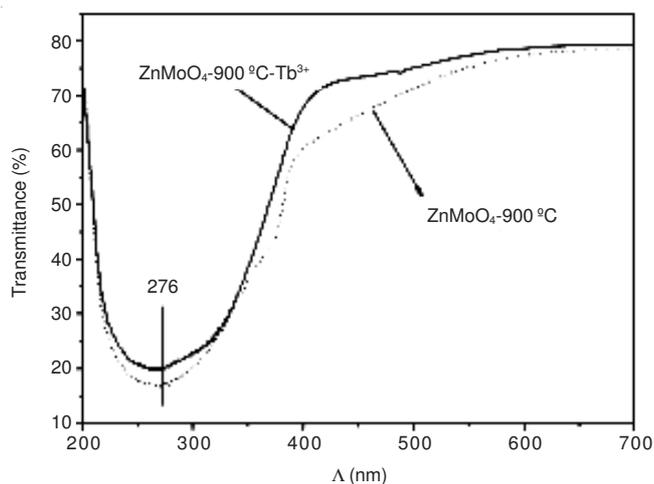


Fig. 4. UV-visible absorption spectra of ZnMoO_4 obtained before and after Tb^{3+} doping

Fig. 5 shows the emission spectra of ZnMoO_4 with 5% Tb^{3+} doping under the excitation at 275 nm. We chose ZnMoO_4 with 5% Tb^{3+} doping to investigate luminescent properties as they have the strongest green light emission by ultraviolet light excitation. The main emission is the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} at 543 nm. Other $f-f$ transitions of Tb^{3+} are weak, such as $^5\text{D}_4 \rightarrow ^7\text{F}_6$ at 489 nm and $^5\text{D}_4 \rightarrow ^7\text{F}_4$ transitions at 583 nm. Under 583 nm, the $^5\text{D}_4 \rightarrow ^7\text{F}_4$ transition having split demonstrates that $\text{ZnMoO}_4:\text{Tb}^{3+}$ has MoO_4^{2-} and Tb^{3+} two luminescent centers. For the sample of ZnMoO_4 doped with 5% Tb^{3+} , the emission intensity of the activation self-luminescent MoO_4^{2-} is weakened greatly, while that of Tb^{3+} $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition at 543 nm (green emission) is significantly enhanced. This phosphor has the potential application value as luminescent material.

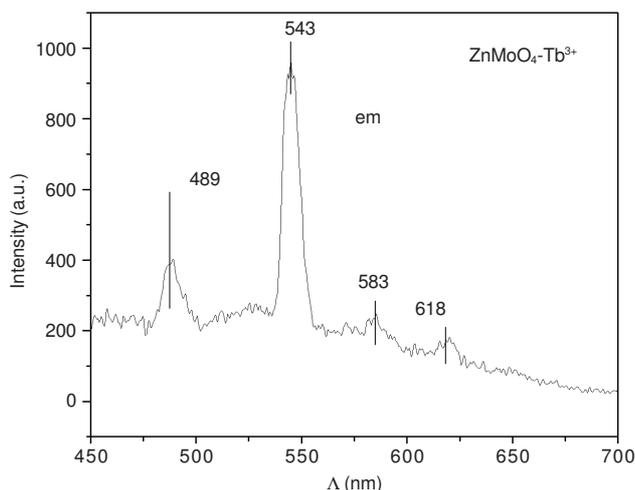


Fig. 5. Emission spectra of ZnMoO_4 with 5% Tb^{3+} doping

Conclusion

We investigated the effect of temperature to the composition and structure of the ZnMoO_4 and $\text{ZnMoO}_4:\text{Tb}^{3+}$ phosphors prepared by the sol-gel method. The strong diffraction peaks in XRD spectra are consistent with the standard spectra when they calcined at 700°C . It is concluded that the single crystalline phase of triclinic structure has been formed completely in the light of this evidence. The morphology of samples observed by SEM show that they have triclinic crystal structure. We also investigated the luminescent properties of $\text{ZnMoO}_4:\text{Tb}^{3+}$ according to emission spectrum, it has strong green light emission when calcined at 900°C . In summary, we can prepare the ultraviolet photoexcitation molybdc acid salt base green phosphors by adjusting the percent of Tb^{3+} .

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REFERENCES

1. X. Li and Z. Zhang, *Chinese J. Rare Earth*, **12**, 69 (2008).
2. X. Li, Y. Yang, Z.P. Yang, L. Guan and C. Liu, *Chinese J. Luminescence*, **29**, 93 (2008).
3. C.F. Guo and T. Chen, *J. Func. Mater.*, **38**, 200 (2007).
4. J. Lin, Q. Su, *Chinese J. Rare Earth*, **2**, 42 (1994).
5. J.B. Yu, X.M. Yuan and J.Z. Chen, *Mater. Rev.*, **15**, 30 (2001).
6. L.D. Zhang and J.M. Mu, *Beijing Sci. Technol. Press*, 135 (2001).
7. Y.S. Yang, J.X. Qi and M.S. Zhang, *J. Inorg. Mater.*, **14**, 20 (1999).
8. Y. Liao, W. Zhu, X.M. Li, Y.Q. Mo, X.G. Hao and X.Q. Ma, *Mater. Rev.*, **21**, 321 (2007).
9. F. Auzel, *Chem. Rev.*, **104**, 139 (2004).