



Synthesis, Characterization and Luminescent Properties of Green Phosphor BaMoO₄:Tb³⁺

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The green phosphor BaMoO₄:Tb³⁺ was prepared by sol-gel method. The effects of doping concentration and sintering temperature on the crystal structure and luminescent properties were investigated by X-ray powder diffraction, scanning electron microscope, UV-visible spectroscopy and photoluminescence spectroscopy. The XRD results showed a pure BaMoO₄ phase can be obtained when calcinating phosphor at 900 °C. The photoluminescence spectroscopy spectra exhibited four peaks, the most intense peak of 542 nm can be attributed to ⁵D₄ → ⁷F₅ transition of Tb³⁺ and the optimized mol percent of Tb³⁺ was 0.05. All the results indicated that BaMoO₄: Tb³⁺ could be used as a white-light emitting diodes ultraviolet photoexcitation green phosphors.

Keywords: BaMoO₄: Tb³⁺, Sol-gel method, Green phosphors.

INTRODUCTION

Light emitting diodes (LED) become the new luminous sources¹ in 21st century and are favored by the markets. To the best of our knowledge, there are three approaches to obtain white light emitting diodes^{2,3}. The first one is multichip method, by mixing red, green, blue lights which were emitted by the corresponding chips in certain percent together. The second one is the integrated single chip method, using a chip to directly emit white light *via* a plurality of active layer. The third one, which was attracted widespread attention for its high luminous efficiency is the fluorescent conversion method, it combines a phosphor with chip. The nature of phosphor plays an important role on the luminescent properties⁴. In recent decades, most of the studies focused on molybdates- or tungstates-based red phosphors, rarely on other colours⁵. MoO₄²⁻ can absorb near ultraviolet light and blue light light emitting diodes and transfer to rare earth ion Tb³⁺⁶. Moreover, Tb³⁺ shows efficient ⁵D₄ → ⁷F₅ transition under the excitation of green light, therefore, we can get green phosphors *via* doping appropriate amount of Tb³⁺ to the molybdates⁷. This method has important significance for the development and application of white light emitting diodes.

The synthesis of molybdate- or tungstate-based phosphors was under high-temperature and solid-state, however some drawbacks are very obvious, such as high reaction temperature, low reaction rate, big size with irregular morphology. On the contrary, the sol-gel method has many advantages, such as

mild reaction conditions, homodisperse, it is quite suitable for synthesize thermal-unstable phosphors. Herein the green phosphor BaMoO₄:Tb³⁺ was prepared by the sol-gel method and its photoluminescence properties were also investigated.

EXPERIMENTAL

Tb(NO₃)₃ (0.1 mol/L), Na₂MoO₄·2H₂O, analytical pure, bought from Tianjin Chemical Plant; BaCl₂·2H₂O, analytical pure, bought from Kaifeng Chemical Plant; HO(CH₂CH₂O)_nH, 6000-7500, Tianjin BASF Chemical.

The structures of samples were characterized by X-ray powder diffraction (XRD, German Bruker with CuK_α radiation, λ = 0.15406 nm). The morphology of nanoparticles were obtained by SEM (FEI Quanta 200 FEG, 40 kV, 150 mA, scan range 15°-65°, scan rate 2°/min). The excitation and emission spectra were recorded by Spectrophotometers (UV-visible Perkin Elmer Lambda35 equipped with an integrating sphere, BaSO₄ was used for the reflection-background contrast; LS55 Fluorescence Spectrometer).

Preparation of the sample BaMoO₄: Firstly, Na₂MoO₄·2H₂O and BaCl₂·2H₂O (stoichiometric ratio = 1:1) were dissolved in deionized water under continuously stirring at room temperature until formed homogeneous solution, then stirred at 40 °C for 0.5 h and filtrated, the transparent gel can be formed. Secondly, the gel was transferred onto a surface plate and maintained at 80 °C in drying oven for 2 h, then it became a white glue. Finally, the white glue was divided into four

portions, placing them in Muffle furnace at 500, 700, 900 and 1100 °C calcined for 4 h, respectively to obtain the final samples.

Preparation of BaMoO₄:Tb³⁺ by the sol-gel method:

At first, 1, 3, 5 and 7 % 0.1 mol L⁻¹ Tb(NO₃)₃ were added into four beakers which contained equal parts of Na₂MoO₄·2H₂O, BaCl₂·2H₂O and polyethylene glycol, respectively and dissolved them in deionized water, then 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 80 °C in drying oven for 2 d, then at 120 °C for 1d to form a light brown gel. At last, the samples were obtained after placing in Muffle furnace at 500, 700 and 900 °C calcined for 4 h.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of BaMoO₄ prepared with different firing temperatures (500, 700, 900 and 1100 °C). As shown in Fig. 1 the sample under firing temperature of 500 °C still had amorphous structure and the crystallinity was also not very good, but the tetragonal BaMoO₄ has been formed basically, the XRD patterns is consistent with JCPDS Card No. 29-0193 ($a = b = 0.558$ nm, $c = 1.283$ nm, $\alpha = \beta = \gamma = 90^\circ$). When the temperature reached to 700 °C, both the width of diffraction peaks and the cell parameters reduced, it indicates that the single crystalline phase of BaMoO₄ sample is becoming better. With the temperature keep rising to 900 °C, the width of the diffraction peak was continue narrowing. And finally when the temperature reached to 1100 °C, the relative intensity of diffraction peaks reduced and part of diffraction peaks disappeared as the high temperature can destroy the phase partly. Therefore, the optimized firing temperature is 700-900 °C.

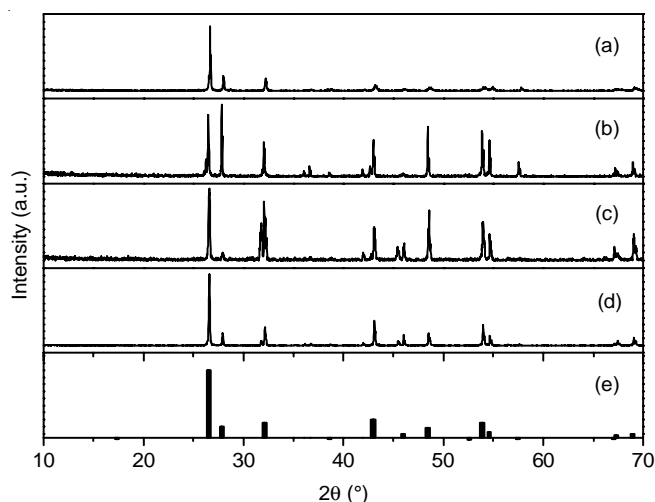


Fig. 1. XRD patterns of the BaMoO₄ samples obtained at different firing temperature; (a) 1100 °C; (b) 900 °C; (c) 700 °C; (d) 500 °C; (e) JCPDS Card

BaMoO₄:Tb³⁺ was obtained when the calcination temperature reached to 900 °C and all the XRD patterns are consistent with JCPDS Card No.29-0193, indicating that the Tb³⁺ doping do not change the tetragonal structure of BaMoO₄ (Fig. 2). The intensity of diffraction peak decreased upon the increased component of the doping, as the Tb³⁺ doping can result in lattice defect.

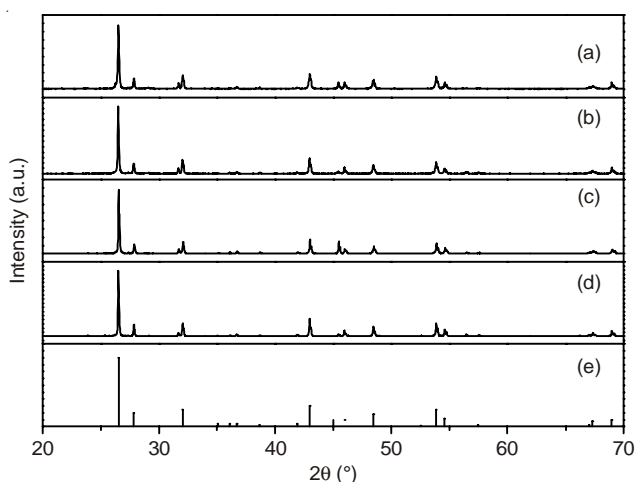


Fig. 2. XRD patterns of the samples BaMoO₄: Tb³⁺ with different doping at 900 °C fired temp; (a) 7 %; (b) 5 %; (c) 3 %; (d) 1 %; (e) BaMoO₄ JCPDS Card

The SEM images of BaMoO₄ prepared by the sol-gel method under different calcining temperatures are shown in Fig. 3. The sample which calcined at 500 °C appears as irregular particles owing to lower temperature reducing the crystallization. With the higher calcining temperature, the surface of the particle become relatively more smooth but still irregular, as shown in Fig. 3 (b). It can be clearly observed that regular small spherical particles are formed when calcined at 900 °C. The particle size is irregular and agglomerate as the temperature reached to 1100 °C in Fig. 3 (d).

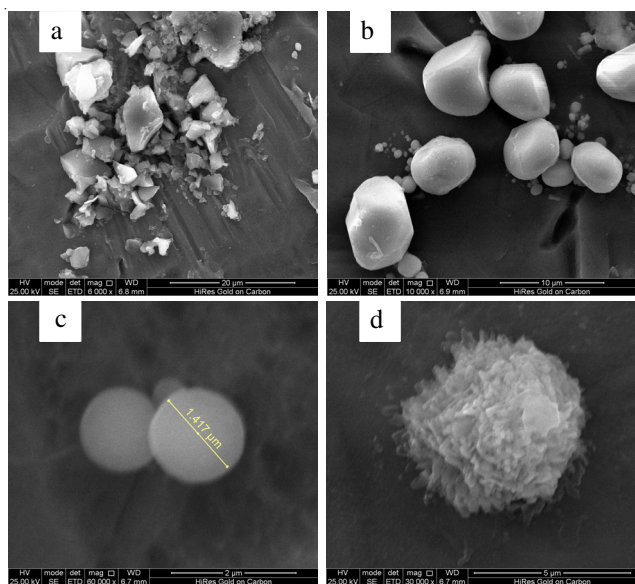


Fig. 3. SEM image of BaMoO₄ fired at 500 (a), 700 (b), 900 (c) and 1100 °C (d)

Fig. 4 shows that the BaMoO₄ has strong absorption at 309 nm no matter whether it calcined at 900 °C for 4 h with Tb³⁺ doping or not, the intensity of undoped sample is slightly higher. Therefore, we can study their luminescent properties *via* the emission spectrum of sample with the excitation of 309 nm.

Fig. 5 represents the emission spectra of the phosphors with different amount of Tb³⁺ doping under 286 nm excitation (the maximum absorption of BaMoO₄ is around 309 nm). The

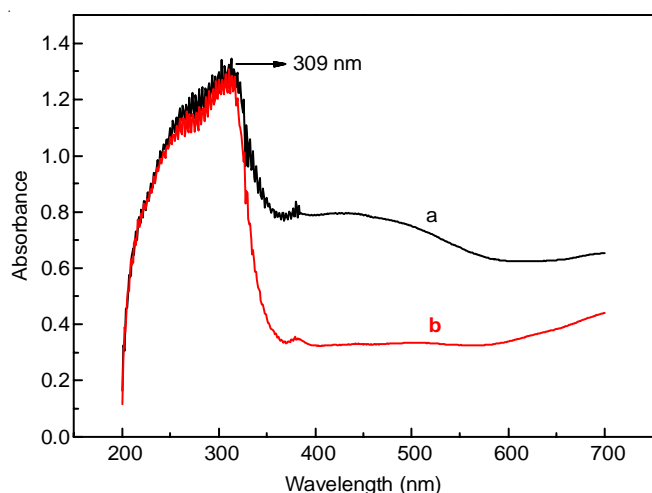


Fig. 4. UV-Visible absorption spectra of BaMoO₄ obtained before and after Tb³⁺ doping; (a) BaMoO₄; (b) BaMoO₄:Tb³⁺

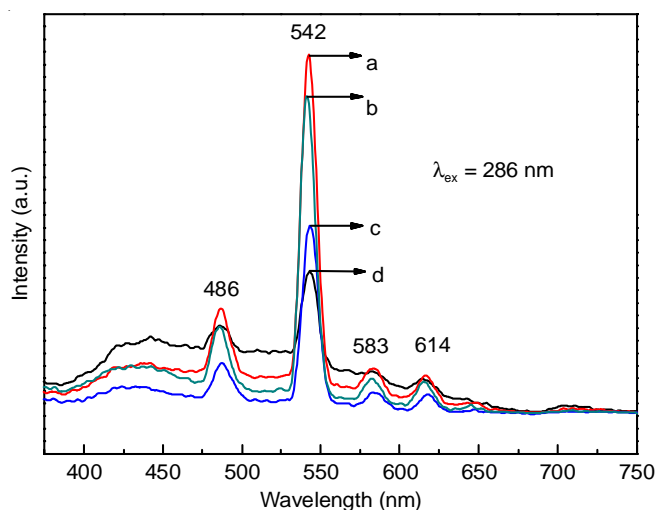


Fig. 5. Photoluminescence spectroscopy spectra of BaMoO₄:Tb³⁺ with different amount of Tb³⁺ doping under 286 nm excitation; (a) 5%; (b) 7%; (c) 3%; (d) 1%

photoluminescence spectroscopy results exhibit four peaks, in which the most intense peak of 542 nm is attributed to ⁵D₄ → ⁷F₅ magnetic dipole transition of Tb³⁺ and the optimized mol percent of Tb³⁺ is 0.05. According to the references, the emission spectra of the sample should exhibit four characteristic peaks at about 486 nm (⁵D₄ → ⁷F₆), 542 nm (⁵D₄ → ⁷F₅), 583 nm (⁵D₄ → ⁷F₄) and 614 nm (⁵D₄ → ⁷F₃).

Conclusion

The green phosphor BaMoO₄:Tb³⁺ was prepared by sol-gel method and the structure, the morphology and the luminescent property were investigated by XRD, SEM and photoluminescence spectroscopy analysis methods. The results of XRD indicated that we got single crystalline phase of BaMoO₄:Tb³⁺ sample under calcinations temperature of 900 °C and regular small spherical particles can be observed *via* SEM spectra. With the increasing of the amount of Tb³⁺, the emission intensity increased firstly and then decreased; and the highest intensity appeared when the proportion of Tb³⁺ is 5%.

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