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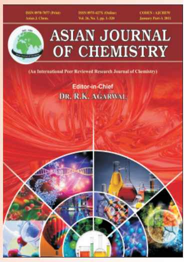

Synthesis and Luminescent Properties of Red Phosphor $Na_{1.8}Zn_{2.1}(MoO_4)_3Eu$ by Sol-Gel Method

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The red phosphor $Na_{1.8}Zn_{2.1}(MoO_4)_3Eu$ was prepared by sol-gel method. The effects of doping concentration and firing temperature on the crystal structure and luminescent properties were investigated by X-ray powder diffraction, scanning electron microscope and fluorescence spectrum. The results indicated that the phosphor exhibited intense red photoluminescence at 610 nm when excited by the light of 464 nm, which was attributed to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}.

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

INTRODUCTION

As known as the new luminous source[1] in 21st century, white light emitting diodes have many advantages[2-5], such as small size, low power consumption, long lifetime, environmental friendly and sensitive characteristics. To our best of knowledge, there are three approaches to obtain white LED[6,7] and the most common method is to combine a yellow-emitting phosphor with blue LED chip[8]. However, there is a problem for such "yellow + blue" white LEDs, which is the absence of red light in this method. Actually the red phosphor plays an important role on the luminescent properties. At present, the commercialized red phosphor $Eu(Y_2O_2S)_3$ has many drawbacks[6-8], such as high cost, no absorption in 400 nm exciting light, low luminous efficiency at near ultraviolet light and blue light areas, unstable and can decompose harmful SO_2 gas. Therefore, it is an important issue to explore a red phosphor which can be excited by near ultraviolet light and blue light.

The luminescent properties of phosphors have close relationship with the original materials and the method of preparation which include high-temperature solid-state reaction, sol-gel method, hydrothermal method, microwave irradiation synthesis, *etc*. Most of the researches focus on the previous two methods. High temperature solid-state reaction has many advantages, such as simple machine, mature technology, high crystallinity. However some drawbacks are also very obvious, such as high reaction temperature, low reaction rate, bigger size with irregular morphology[9,10]. Hydrothermal method was only used to prepare oxide and sulfide which were not sensitive to water. Herein a sol-gel method was reported to prepare red phosphor, it has many advantages, such as mild reaction conditions, homodisperse, suitable for synthesize thermal-unstable phosphor, *etc*.

The molybdate phosphors are very stable and have intensive and broaden charge transfer absoprtion band at near ultraviolet area, thus they are considered to be a promising phosphor materials[11]. Eu^{3+} is an important activator of red phosphor, when Eu^{3+} located on the inversion symmetry position of fluorescent materials. It can produce long wavelength emission at around 615 nm, which is attributed to $^5D_0 \rightarrow {}^7F_2$ transition. Molybdate Eu^{3+} has strong absorption of *f-f* transition and the $^7F_0 \rightarrow {}^5L_6$ absorption at near ultraviolet area, around 395 nm, which coincide with the emission of near ultraviolet LED[12], thus these phosphor may be a better candidate for red emitting phosphor for the white LED. Therefore, study of Eu^{3+}-doped molybdate phosphor[12,13] has important significance for the development and application of white LED. In present paper the phosphor $Na_{1.8}Zn_{2.1}(MoO_4)_3Eu$ was prepared by the sol-gel method and its photo-luminescence properties were investigated.

EXPERIMENTAL

0.1 mol/L $Eu(NO_3)_3$; $Na_2MoO_4{\cdot}2H_2O$, analytical pure, bought from Tianjin Chemical Plant; $ZnCl_2$, analytical pure, bought from Tianjin Chemical Plant; $HO(CH_2CH_2O)nH$, 6000-7500, Tianjin BASF Chemical.

Preparation of $Na_{1.8}Zn_{2.1}(MoO_4)_3Eu$ by the sol-gel method: First, 2.4246 g $Na_2MoO_4{\cdot}2H_2O$ and 1.7442 g $ZnCl_2$

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 0.5 h and filtrated. Secondly, the gel was transferred onto a surface plate and maintained at 80 °C in drying oven for 2 h to form white gel and then divided into six parts. Finally, the samples were obtained after placing in Muffle furnace at 100, 200, 300, 400, 500 and 600 °C fired for 4 h, respectively.

Firstly, 1 mL, 3 mL, 5 mL, 7 mL, 10 mL, 12 mL 0.1 mol L^{-1} $Eu(NO_3)_3$ were added into six beakers which contain equal parts of 2.4246 g $Na_2MoO_4·2H_2O$, 1.7442 g $ZnCl_2$ and 0.4625 g polyethylene glycol respectively, then add deionized water. The transparent gel was formed after stirred at 40 °C for 0.5 h and filtrated. Secondly, the gel was transferred onto a surface plate and maintained at 80 °C in drying oven until to form a white gel. At last, the samples were obtained after placing in Muffle furnace at optimized temperature fired for 4 h.

Characterization: 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, $BaSO_4$ was used for the reflection-background contrast; LS55 Fluorescence Spectrometer).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of $Na_{1.8}Zn_{2.1}(MoO_4)_3$ prepared by sol-gel method with different firing temperature (300 °C, 400 °C, 500 °C) for 4 h. As shown in Fig. 1 the sample under firing temperature of 300 °C still has amorphous structure and the crystallinity is not very good, yet the $Na_{1.8}Zn_{2.1}(MoO_4)_3$ has been formed basically and the XRD patterns are consistent with PDF#32-1209. When the temperature rises to 400 °C, the relative intensity of diffraction peak is increased while the width reduced, which shows that the single crystalline phase of $Na_{1.8}Zn_{2.1}(MoO_4)_3$ sample is becoming well; when the temperature rising to 500 °C, although the width of the diffraction peak is changed with some mixed peaks appeared, yet the the XRD patterns are mostly consistent with PDF#32-1209. Therefore, the optimized firing temperature is 400 °C.

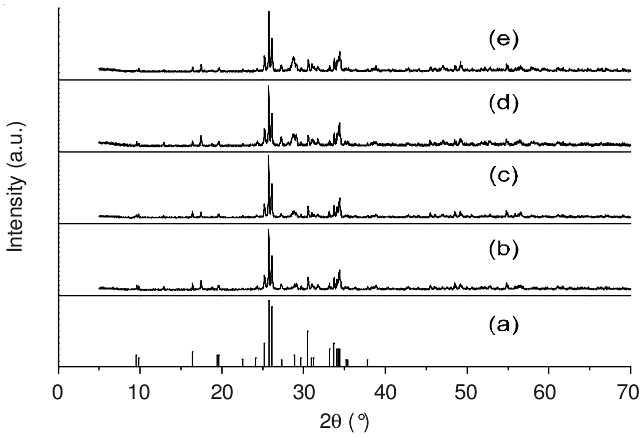

Fig. 1. XRD patterns of the $Na_{1.8}Zn_{2.1}(MoO_4)_3$ samples obtained at different firing temp. (a) PDF#32-1209; (b) 300 °C; (c) 400 °C; (d) 500 °C; (e) 600 °C

$NaZn_2OH(MoO_4)_2(H_2O)$ was obtained when the calcinations temperature is 100 °C and the XRD patterns are consistent with PDF#70-0161. With the temperature rising to 200 °C, although some mixed peaks appear, yet the the XRD patterns are mostly consistent with PDF#70-0161. But the amorphous structure begins to change, with the result of (Fig.1), the sample becomes to $Na_{1.8}Zn_{2.1}(MoO_4)_3$ when the firing temperature up to 300 °C. The results of Figs. 1 and 2 indicate that the sample $NaZn_2OH(MoO_4)_2(H_2O)$ transforms to $Na_{1.8}Zn_{2.1}(MoO_4)_3$ due to dehydrate with higher temperature.

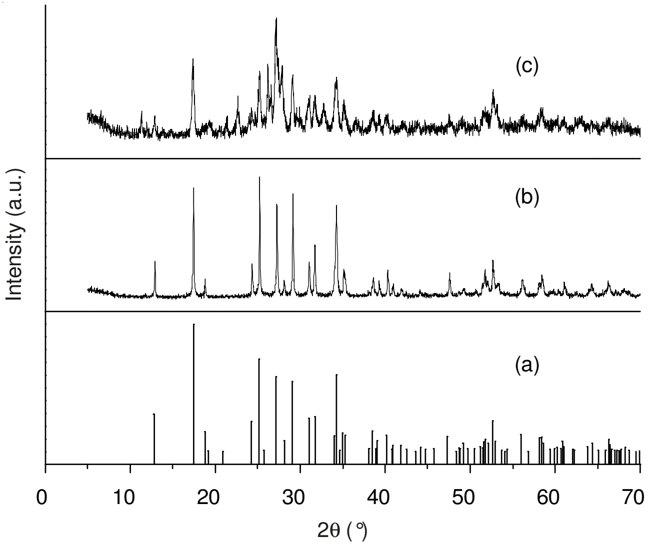

Fig. 2. XRD patterns of the $NaZn_2OH(MoO_4)_2(H_2O)$ samples obtained at different firing temp. (a) PDF#70-0161; (b) 100 °C; (c) 200 °C

Fig. 3 is X-ray diffraction patterns of the samples $Na_{1.8}Zn_{2.1}(MoO_4)_3$ with different amount of Eu^{3+} doping fired at 400 °C. There are some mixed peaks appeared after Eu^{3+} doped. but the shapes of peaks are mostly unchanged, which indicate Eu^{3+} doping does not effect the formation of $Na_{1.8}Zn_{2.1}(MoO_4)_3$.

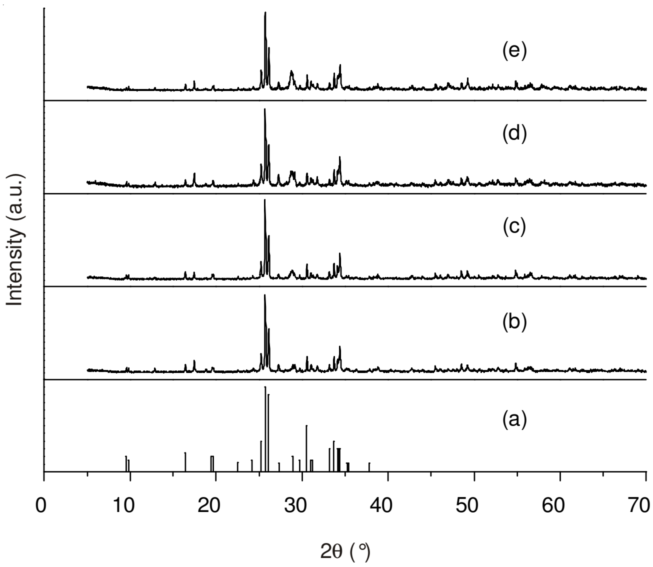

Fig. 3. XRD patterns of the samples $Na_{1.8}Zn_{2.1}(MoO_4)_3$ with Eu^{3+} doping at 400 °C fired temp (a) PDF#32-1209; (b) 1 %; (c) 3 %; (d) 5 %; (e) 7%

Figs. 4 and 5 demonstrate that the $Na_{1.8}Zn_{2.1}(MoO_4)_3$ has strong absorption at about 315 nm and weak absorption at about 364 nm under the 400 °C calcination, no matter whether with Eu^{3+} doping or not, it has absorption at about 362 nm as well.

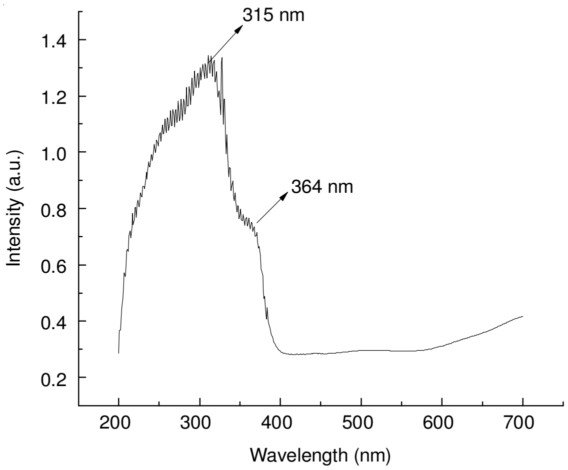

Fig. 4. UV-visible absorption spectra of $Na_{1.8}Zn_{2.1}(MoO_4)_3$

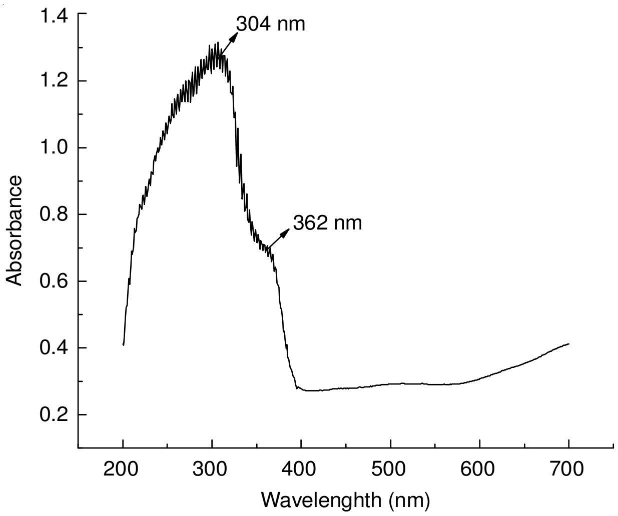

Fig. 5. UV-visible absorption spectra of $Na_{1.8}Zn_{2.1}(MoO_4)_3$: Eu^{3+}

The excitation spectra of red phosphor $Na_{1.8}Zn_{2.1}(MoO_4)_3$: Eu^{3+} is shown in Fig. 6. It has strong absorption at short wavelength areas, for example, ultraviolet light (285 nm), near ultraviolet light (394 nm) and blue light (464 nm). The maximum wavelength of emission spectra is 616 nm, which coincide with the emitting light of near ultraviolet and blue LED chip, thus these phosphor may be the better candidate for red emitting phosphor for the white LED.

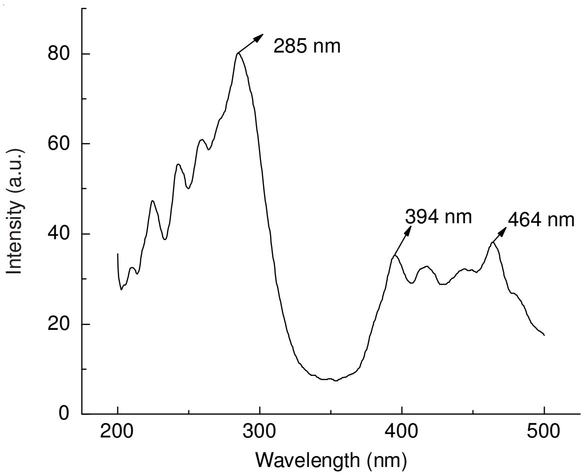

Fig. 6. Excitation spectrum of $Na_{1.8}Zn_{2.1}(MoO_4)_3$: Eu^{3+}

Fig. 7 represents the emission spectra of the phosphors with different amount of Eu^{3+} doping under 464 nm excitation. With the increasing of the amount of Eu^{3+}, the emission intensity is increased. The intensity reaches maximum when the doping amount of Eu^{3+} up to 7 % and then reduces if the amount of Eu^{3+} continues to increase. According to the reference, the emission spectra of the sample exhibit sharp peaks at about 590 nm, 615 nm and 622 nm, which belong to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ transitions for the two peaks of 590 nm and 615 nm respectively. According to the theory of 4*f* transition of rare earth ion, only magnetic dipole transition is allowed when the rare earth ion having inversion center site, on the contrary, forced electric dipole transition is allowed. The transition of $^5D_0 \rightarrow {}^7F_2$ is stronger than $^5D_0 \rightarrow {}^7F_1$, which indicates that Eu^{3+} is occupied the inversion symmetry center.

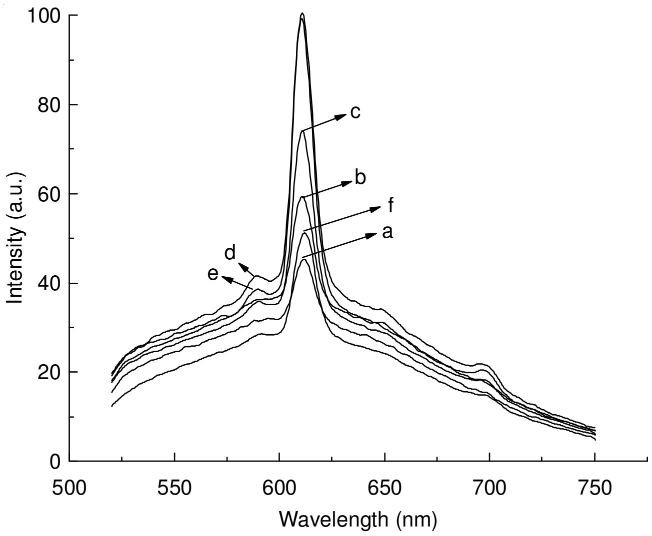

Fig. 7. Emission spectra of $Na_{1.8}Zn_{2.1}(MoO_4)_3$: Eu^{3+} with different amount of Eu^{3+} doping under 464 nm excitation (a) 1 %; (b) 3 %; (c) 5 %; (d) 7 %; (e) 10 %; (f) 12 %

The SEM image of $Na_{1.8}Zn_{2.1}(MoO_4)_3$ prepared by the Sol-Gel method with calcinations temperature of 400 °C is shown in Fig. 8(a). It has numerous irregular crystals stucked by sol. At 500 °C, the sol was sintered and thus we can observe dispersed irregular crystals in Fig. 8(b). The SEM image of $Na_{1.8}Zn_{2.1}(MoO_4)_3$: Eu^{3+} 7 % fired at 400 °C is shown in Fig. 8(c), the particle size is irregular and agglomerate.

Conclusion

The red phosphor $Na_{1.8}Zn_{2.1}(MoO_4)_3Eu$ was prepared by sol-gel method and its structure, the morphology and the luminescent property were investigated by XRD, SEM and photoluminescence analysis methods. The results of XRD indicate the single crystalline phase of $Na_{1.8}Zn_{2.1}(MoO_4)_3$ sample under calcinations temperature of 400 °C. It has been found that $Na_{1.8}Zn_{2.1}(MoO_4)_3$ can emit red light with the excitation of 394 nm and 464 nm lights and the maximum emission peak is 616 nm, which coincide with the emitting light of near ultraviolet and blue LED chips, thus these phosphor may be the better candidate for red emitting phosphor for the white LED. With the increasing of the amount of Eu^{3+}, the emission intensity is increased first and then reduced; when up to 7 %, the intensity is the highest. When the amount of Eu^{3+} up to 12 %, we observe the concentration quenching.

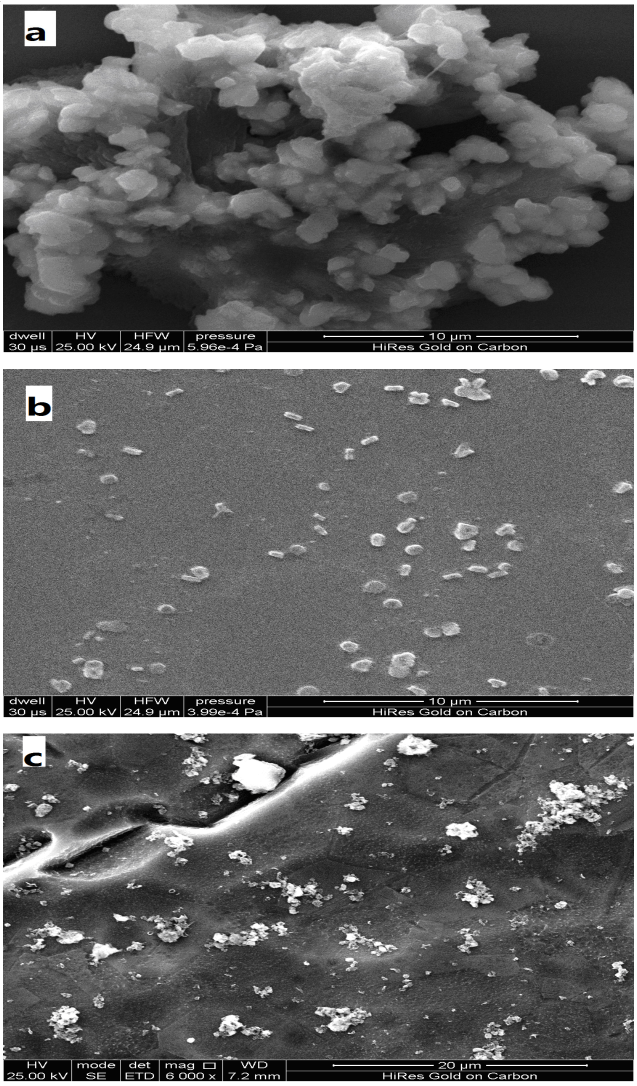

Fig. 8. SEM images of $Na_{1.8}Zn_{2.1}(MoO_4)_3$ fired at 400 °C (a) 500 °C (b) and $Na_{1.8}Zn_{2.1}(MoO_4)_3$: Eu^{3+} 7 % fired at 400 °C (c)

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