



## Preparation and Luminescent Properties of White Light-Emitting Single-Phased Phosphor $\text{ZnWO}_4:\text{Eu}^{3+}$

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The white light-emitting  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors were synthesized by hydrothermal process followed by calcination at different temperatures. The phase structure, morphology and luminescent properties of the as-synthesized samples were characterized by X-ray diffraction, scanning electron microscope and fluorescence spectrophotometer. The results indicate that all the  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors are pure monoclinic structure. The  $\text{ZnWO}_4:\text{Eu}^{3+}$  samples are spherical nanoparticles and the particle size significantly grows with increasing calcination temperature. The emission spectrum of  $\text{ZnWO}_4:\text{Eu}^{3+}$  is composed of the broad band attributing to the intrinsic emission of  $\text{WO}_4^{2-}$  and a series of sharp emission peaks originating from the characteristic emission of  $\text{Eu}^{3+}$ . The luminescent intensities of the samples are gradually improved with the increase of calcination temperature. Moreover, all of the  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  phosphors emit white light and the color coordinate of  $\text{Zn}_{0.98}\text{WO}_4:\text{Eu}^{3+0.02}$  phosphor is very close to the standard white chromaticity.

**Keywords:** White light-emitting diodes,  $\text{ZnWO}_4:\text{Eu}^{3+}$ , Phosphor, Luminescence.

### INTRODUCTION

White light-emitting diodes have attracted extensive attention due to the merits of low energy consumption, high efficiency, long service life, good stability and environmental protection compared with the traditional incandescent and fluorescent lamps<sup>1-4</sup>. At present, commercial white light-emitting diodes, composed of a blue light light-emitting diode chip with a yellow-emitting phosphor  $\text{YAG}:\text{Ce}^5$ , have some defects like low color-rendering index and high color temperature, due to the lack of red-emitting component. Another method to generate white light is the combination of a UV-LED or NUV-LED chip with the three-phased phosphors of red, green and blue<sup>6,7</sup>. However, this kind of white light-emitting diodes is of low luminous efficiency as the result of the re-absorption of emission colors. To solve the above problems, the single-phased white-emitting phosphors<sup>8-11</sup> become a better choice, which can be excited effectively by a UV-LED or NUV-LED chip to fabricate white light and are characterized with the properties of good stability and high luminous efficiency.

As a type of single-phased white-emitting phosphors,  $\text{ZnWO}_4:\text{Eu}^{3+}$  will emit white light, by combining the blue-green light exhibited by  $\text{WO}_4^{2-}$  and red light emitted by  $\text{Eu}^{3+}$ . Therefore,  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors can be potentially used in white light-emitting diodes.

Recently,  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors have been synthesized through various methods. Dong *et al.*<sup>12</sup> synthesized the  $\text{Eu}^{3+}$ -

doped  $\text{ZnWO}_4$  using self-propagating combustion method; Yan *et al.*<sup>13</sup> prepared the  $\text{ZnWO}_4:\text{Eu}^{3+}$  nanophosphors adopting molten salt method; Dai *et al.*<sup>14</sup> synthesized the  $\text{ZnWO}_4:\text{Eu}^{3+}$  nanocrystals by the hydrothermal route at different pH values and hydrothermal temperatures. Usually, it is difficult to control the morphology and enhance the luminescence properties of the rare earth doped phosphors at the same time by these methods.

In present study, the  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors were prepared by hydrothermal process followed by calcination. The morphology can be well controlled by hydrothermal process and the luminescence intensity of the phosphors can be enhanced by calcination. Besides, the effects of calcination temperature and  $\text{Eu}^{3+}$  concentration on phase structure, morphology and luminescence properties of the as-synthesized  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors were analyzed. Moreover, a tunable bright white light-emitting was realized by adjusting the  $\text{Eu}^{3+}$  concentration.

### EXPERIMENTAL

The  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors were synthesized by hydrothermal process followed by calcining at different temperatures. The starting materials were  $\text{Eu}_2\text{O}_3$  (99.99 %),  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (A.R.),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (A.R.),  $\text{HNO}_3$  (A.R.) and  $\text{NaOH}$  (A.R.). First, aqueous solution of  $\text{Eu}(\text{NO}_3)_3$  was prepared by dissolving  $\text{Eu}_2\text{O}_3$  in a certain amount of nitric

acid. Depending on the stoichiometric ratio of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  ( $x = 0.5, 2, 4, 6$  mol. %) phosphors, appropriate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Eu}(\text{NO}_3)_3$  solution were added into 20 mL deionized water with stirring to make the nitrate solution mix uniformly. Next, 7 mmol  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved in 30 mL deionized water and then the prepared  $\text{Na}_2\text{WO}_4$  solution was added dropwise into the above mixed nitrate solutions under constant magnetic stirring. White suspension was formed. Then the pH value of the reaction system was adjusted to 6 by adding NaOH solution. After stirring for 30 min, the mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave with a filling capacity of 80 %. The autoclave was sealed and maintained at 180 °C for 12 h in an oven. After air-cooled to room temperature, the as-synthesized white precipitates were filtered and washed, respectively with deionized water and absolute ethanol three times and then dried at 90 °C for 6 h to obtain hydrothermal products. Finally, the hydrothermal products were calcined at different temperatures (600, 700 and 800 °C) for 1 h in a muffle furnace. After the products were cooled to room temperature in the furnace, the target products were obtained by grinding.

Phase structure and crystallization of the samples were carried out on a Y-2000 X-ray powder diffraction (XRD) with  $\text{CuK}\alpha$  radiation (30 kV  $\times$  20 mA and  $\lambda = 1.54178 \text{ \AA}$ ). The morphology of the phosphors was analyzed with a JSM-7500F field emission scanning electron microscopy (FE-SEM). Fluorescence spectra of the samples were measured on an F-380 fluorescence spectrometer and the excitation and emission slits were 10 nm and 5 nm, respectively. All measurements were conducted at room temperature.

## RESULTS AND DISCUSSION

**XRD analysis:** Fig. 1 shows the XRD patterns of the  $\text{ZnWO}_4:\text{Eu}^{3+}$  hydrothermal product without calcination and the samples obtained from calcining hydrothermal product at 600, 700 and 800 °C for 1 h, respectively. It can be seen that all of the diffraction data can be matched well with the standard card of  $\text{ZnWO}_4$  (JCPDS No. 15-0774), which indicates that the samples are pure monoclinic wolframite structure with space group P2/c. From Fig. 1, it also can be observed that the

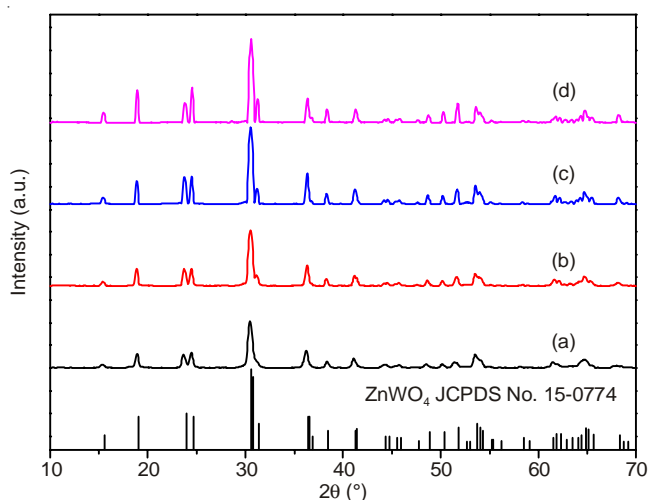


Fig. 1. XRD patterns of  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors without calcination (a); calcined at 600 °C (b), 700 °C (c) and 800 °C (d)

hydrothermal product without calcination is already the pure phase  $\text{ZnWO}_4:\text{Eu}^{3+}$ , but the intensity of diffraction peaks is weak and the peaks are broad, revealing that the crystallinity is relatively low. By calcining, the intensity of diffraction peaks is significantly improved and increases gradually with increasing calcination temperature. Meanwhile, the diffraction peaks become sharper, which indicates that the crystallinity of  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors are enhanced gradually.

**SEM and EDS analysis:** To investigate the effect of calcination temperature on the morphology of the samples, the SEM analysis was conducted. Fig. 2a,b present the SEM images of the  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors before calcining and calcined at 700 °C. It can be seen that  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors are composed of small spherical particles. Before calcination, the diameter of spherical particles is about 60-80 nm. After  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphor was calcined at 700 °C, the size of the particles is significantly increased. The diameter is about 110-135 nm. The result indicates that the calcination process leads to the growth of nanoparticles.

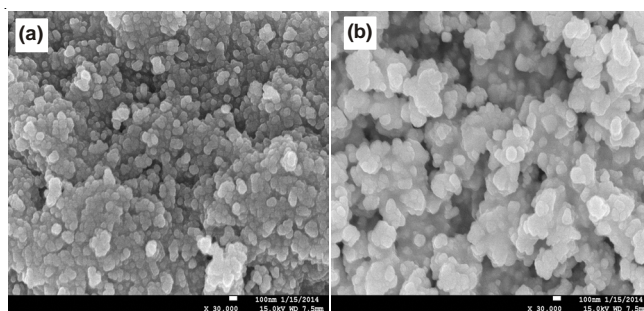


Fig. 2. SEM images of  $\text{ZnWO}_4:\text{Eu}^{3+}$  (a) before calcining; (b) calcined at 700 °C

Fig. 3 shows the energy dispersive spectrometry (EDS) pattern of the  $\text{ZnWO}_4:\text{Eu}^{3+}$  hydrothermal product. It can be seen that the product consists of W, Zn, O and also Eu elements, which indicates that  $\text{Eu}^{3+}$  ions have been introduced into the  $\text{ZnWO}_4$  host lattice. This conclusion is consistent with the XRD result.

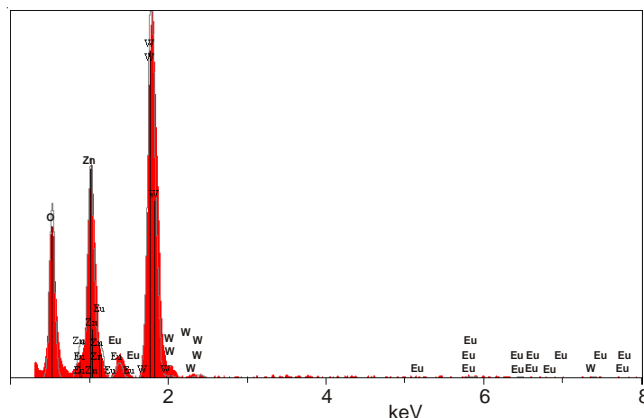


Fig. 3. EDS pattern of  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphor

**Excitation and emission spectrum:** For the series of  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors synthesized under different conditions, the shape of excitation and emission spectra are similar. The  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$  hydrothermal product is taken as an example. Its excitation and emission spectra are shown in Fig. 4. It can

be seen that the excitation spectrum (left part) not only includes a broad band extending from 220 to 350 nm with the peak wavelength at 295 nm, but also a series of sharp peaks in range of 350 to 500 nm. The broad band is ascribed to the charge transfer transition of W-O and Eu-O. The sharp peaks are attributed to the  $f-f$  transition of  $\text{Eu}^{3+}$  and the strong peaks located at 395 and 465 nm are corresponding to  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  and  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  transition of  $\text{Eu}^{3+}$ , respectively. The strongest excitation peak of the phosphor is located at 295 nm, so 295 nm is chosen as the excitation wavelength. As shown in Fig. 4 (right part), the emission spectrum is composed of the broad band between 350 and 550 nm and the sharp peaks in range of 550 to 700 nm. The broad band is attributed to the intrinsic emission of  $\text{WO}_4^{2-}$ . The sharp peaks are originated from the characteristic emission of  $\text{Eu}^{3+}$ , among which three peaks located at 594 nm, 616 and 658 nm are ascribed to the magnetic dipole transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ , the electronic dipole transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and radiative transition of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ , respectively<sup>15</sup>. And the peak at 616 nm corresponding to the red-emitting is strongest. Under the excitation of UV-light,  $\text{ZnWO}_4$  host emits blue-green light and the  $\text{Eu}^{3+}$  ions in  $\text{ZnWO}_4$  host show red-emitting, so the phosphors will emit bright white light by combining the two parts of emissions.

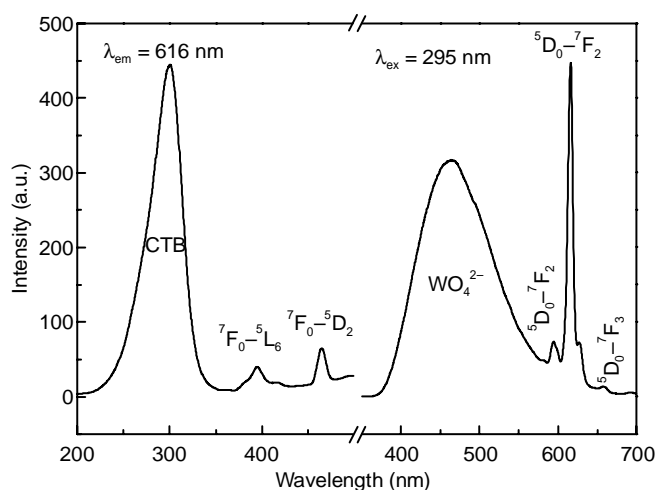


Fig. 4. Excitation spectrum (left) and emission spectrum (right) of  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$

**Effect of calcination temperature on luminescent properties:** Fig. 5 shows the emission spectra of  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$  hydrothermal product without calcination and the samples obtained from calcining hydrothermal product at 600, 700 and 800 °C, respectively. It can be seen that the emission band and peaks of hydrothermal product are relatively weak. After calcining, the shape and position of band or peaks have no considerable change, but the intensity is significantly enhanced and grows gradually with the increase of calcination temperature. The reason is that after calcination, the crystallinity of phosphors increases (Fig. 1) and the surface defects of particles decrease, resulting in a reduction in the number of non-radiative transition and then an enhancement of the emission intensity. As the calcination temperature increases, crystallization tends to be more perfect (Fig. 1). Therefore the luminescent intensity strengthens gradually.

As shown in Fig. 5, after calcination, the intensity of the broad emission band of  $\text{ZnWO}_4$  host is much higher than that of the emission peaks of  $\text{Eu}^{3+}$  ions. This may be because after calcination, the efficient energy transfers from  $\text{WO}_4^{2-}$  ions to  $\text{Eu}^{3+}$  ions in  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors decrease<sup>16</sup>.

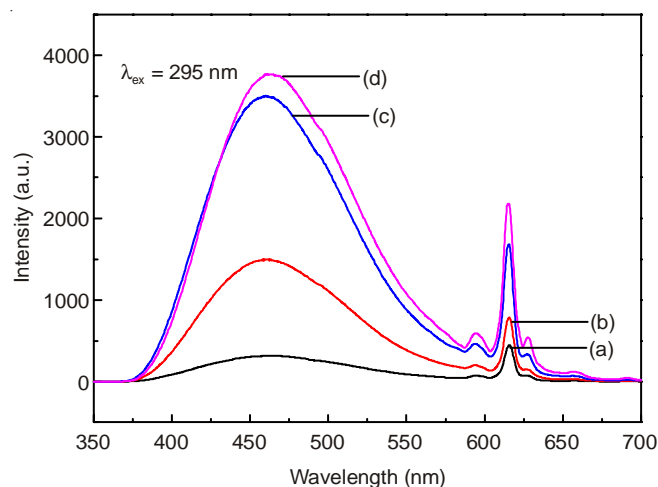


Fig. 5. Emission spectra of  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$  phosphors without calcination (a); calcined at 600 °C (b), 700 °C (c) and 800 °C (d)

Fig. 6 presents the CIE (Commission Internationale de L'Eclairage, 1931) chromaticity diagram of  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$  phosphors before and after calcination. The  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$  hydrothermal product calcined at 700 °C is taken as an example. It can be seen that  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$  phosphors before and after calcining at 700 °C emit warm white and cool white light, respectively. The reason is that the phosphor emits the composite color warm white light before calcining, since the emission intensity of  $\text{WO}_4^{2-}$  (blue-green region) is weaker than that of  $\text{Eu}^{3+}$  (red region). After calcination, the phosphor exhibits the composite color cool white light as the emission intensity of  $\text{WO}_4^{2-}$  is significantly stronger than that of  $\text{Eu}^{3+}$ .

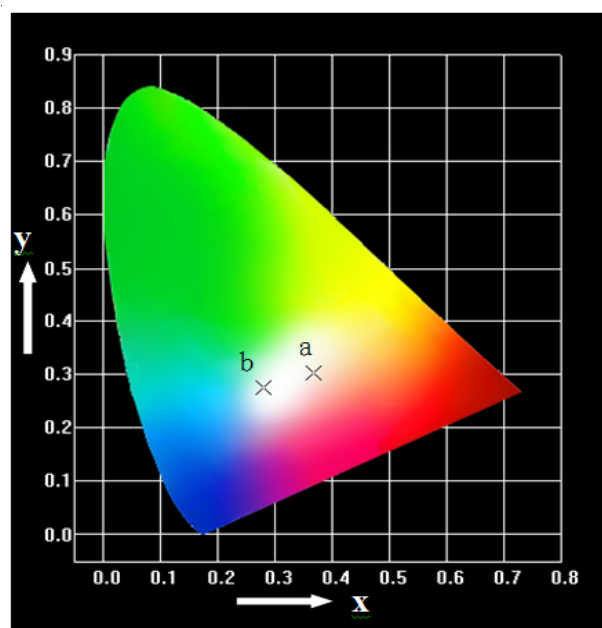


Fig. 6. CIE chromaticity diagram of  $\text{Zn}_{0.995}\text{WO}_4:\text{Eu}^{3+}_{0.005}$  phosphors (a) without calcination; (b) calcined at 700 °C

**Effect of  $\text{Eu}^{3+}$  concentration on luminescent properties:**

Fig. 7a shows a series of emission spectra of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  ( $x = 0.5, 2, 4, 6$  mol %) phosphors calcined at  $700^\circ\text{C}$ . It is obvious that the shape and position of the emission spectra have no visible change as the  $\text{Eu}^{3+}$  concentration increases. As shown in Fig. 7a, at first, the emission intensity of  $\text{WO}_4^{2-}$  decreases remarkably with the increase of  $\text{Eu}^{3+}$  concentration. When the  $\text{Eu}^{3+}$  concentration reaches 4 mol %, the emission intensity of  $\text{WO}_4^{2-}$  turns lowest. However, the emission intensity increases again when the  $\text{Eu}^{3+}$  concentration is more than 4 mol %. The reason is that there exists not only the energy transfer from  $\text{WO}_4^{2-}$  to  $\text{Eu}^{3+}$  but also the reverse transfer from  $\text{Eu}^{3+}$  to  $\text{WO}_4^{2-}$ . Fig. 7b presents the variation of emission intensity of  $\text{Eu}^{3+}$  (at 616 nm) with different  $\text{Eu}^{3+}$  concentration, it can be seen that the emission intensity of  $\text{Eu}^{3+}$  increases gradually with the increasing  $\text{Eu}^{3+}$  concentration from 0.5 to 2 mol % and reaches the maximum at  $x = 2$  mol %. When the  $\text{Eu}^{3+}$  concentration is more than 2 mol %, the intensity decreases gradually, which is the concentration quenching phenomenon<sup>17</sup>. This is because when the  $\text{Eu}^{3+}$  concentration reaches a certain value, the interaction between  $\text{Eu}^{3+}$  ions increases and energy transfer generates, which results in the increase of the probability of non-radiative transitions and leads to the decreased emission intensity of  $\text{Eu}^{3+}$ .

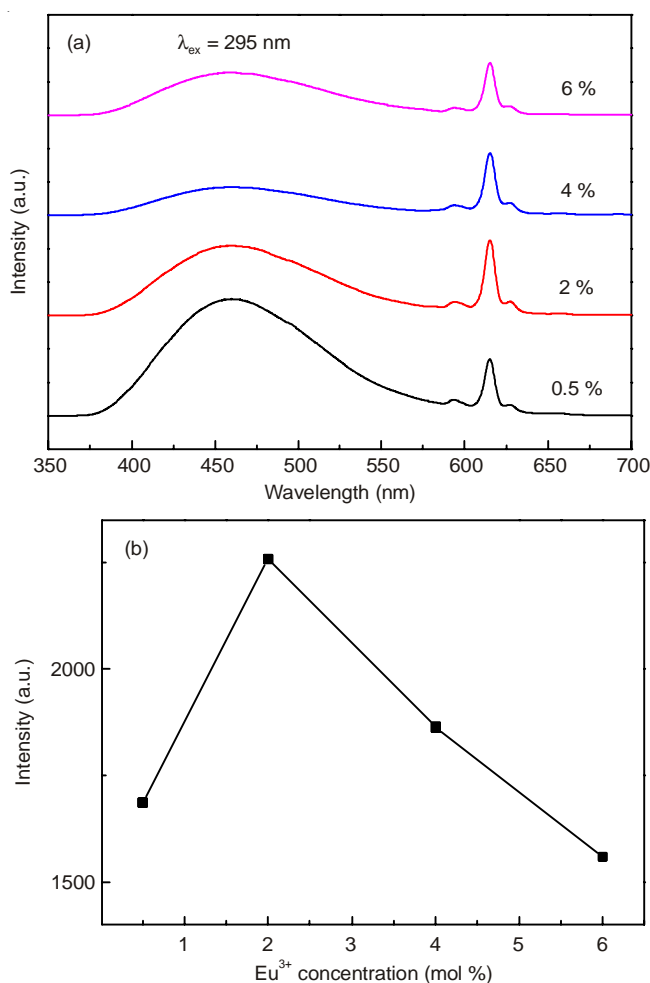


Fig. 7. (a) Emission spectra of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  phosphors calcined at  $700^\circ\text{C}$ ; (b) variation of emission intensity of  $\text{Eu}^{3+}$  with different  $\text{Eu}^{3+}$  concentration

Table-1 presents the color coordinates and color temperature of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  ( $x = 0.5, 2, 4, 6$  mol %) phosphors calcined at  $700^\circ\text{C}$  under the UV-light excitation at 254 nm. It can be seen that the color coordinate of  $\text{Zn}_{0.98}\text{WO}_4:\text{Eu}^{3+0.02}$  phosphor ( $x = 0.3295, y = 0.2818$ ) at the color temperature of 5780 K is very close to the standard white chromaticity ( $x = 0.33, y = 0.33$ ) for the National Television Standard Committee (NTSC) system<sup>18</sup>. In order to clearly observe the color change of the  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  phosphors with the different  $\text{Eu}^{3+}$  concentration, the CIE chromaticity diagram was studied. The CIE diagram (Fig. 8) presents that all the color coordinates of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  phosphors are located in white light zone. The color of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  phosphors shifts from cool white region (point a) through white region (point b) and finally to warm white light region (point c, d) as the  $\text{Eu}^{3+}$  concentration increases. So it is clear that the color coordinates of phosphors can be adjusted by changing the  $\text{Eu}^{3+}$  concentration. Therefore, the series of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  phosphors can be potentially applied in white lighting-emitting diodes (W-LEDs).

TABLE-1  
COLOR COORDINATES AND COLOR  
TEMPERATURE OF  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  PHOSPHORS

$\text{Eu}^{3+}$ concentration (x) (mol %)	Color coordinates	Color temperature (K)
0.5 (a)	(0.2810, 0.2751)	10933
2 (b)	(0.3295, 0.2818)	5780
4 (c)	(0.3864, 0.2871)	2846
6 (d)	(0.3663, 0.2883)	3577

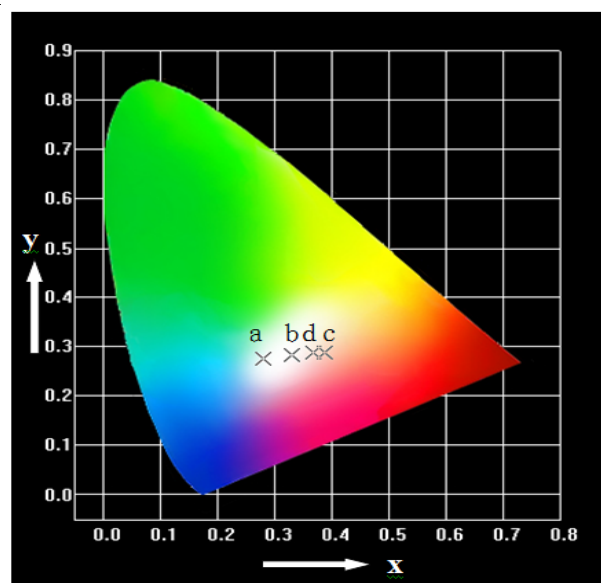


Fig. 8. CIE chromaticity diagram of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+x}$  ( $x = 0.5, 2, 4, 6$  mol %) phosphors calcined at  $700^\circ\text{C}$

**Conclusion**

The  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors were synthesized by hydrothermal process followed by calcining at different temperatures. All the as-synthesized  $\text{ZnWO}_4:\text{Eu}^{3+}$  phosphors have the pure monoclinic phase with space group  $P2_1/c$ . The sample has better crystallinity with increasing calcination temperature. The particles of phosphors are spherical in shape and the size grows as the calcination temperature increases. As for the

samples  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+}_x$  ( $x = 0.5, 2, 4, 6$  mol %), the blue-green emission intensity of  $\text{WO}_4^{2-}$  first decreases and then increases with the increase of  $\text{Eu}^{3+}$  concentration. When the  $\text{Eu}^{3+}$  concentration reaches 4 mol %, the emission intensity of  $\text{WO}_4^{2-}$  becomes lowest. However, the red emission intensity of  $\text{Eu}^{3+}$  shows the opposite trend as the  $\text{Eu}^{3+}$  concentration increases and emission intensity reaches the strongest when the  $\text{Eu}^{3+}$  concentration is 2 mol %. Therefore, the photoluminescence color of  $\text{Zn}_{1-x}\text{WO}_4:\text{Eu}^{3+}_x$  phosphors can be tuned from cool white, white to warm white by adjusting the doping concentrations of  $\text{Eu}^{3+}$ . In particular, the color coordinate of  $\text{Zn}_{0.98}\text{WO}_4:\text{Eu}^{3+}_{0.02}$  phosphor is very close to the standard white chromaticity, so  $\text{ZnWO}_4:\text{Eu}^{3+}$  can be a potential white phosphor used in light-emitting diodes.

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