# Effect of Sintering Temperature, Sm<sup>3+</sup> Concentration and Excitation Wavelength on Luminescence Properties in Eu<sup>3+</sup> Doped Strontium Tungstate Phosphors

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The color-tunable SrWO4:0.20Eu<sup>3+</sup>, Sm<sup>3+</sup> phosphors are successfully prepared by co-precipitation method at a low temperature (800 °C). These phosphors can be efficiently excited by near-ultraviolet and blue light. The phase formation, luminescence properties, energy transfer between Eu<sup>3+</sup> and Sm<sup>3+</sup>, and the critical distance were studied. The Sm<sup>3+</sup> ions as the sensitizer could extend the excitation spectrum and enhance emission. The CIE chromaticity coordinate was also presented. The emission hues covered the regions from pink, orange, to reddish-orange, and eventually to red, which can be controlled by adjusting excitation energy, calcination temperature, and doping rare earth ions ratio via the energy transfer. The high efficiency and high color purity red emitting SrWO4:0.20Eu<sup>3+</sup>, xSm<sup>3+</sup> (x = 0.005 ÷ 0.01) phosphors have higher color saturation than the commercially available Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> red phosphor, which is in coincidence with the National Television Standard Committee system standard for red chromaticity (0.67, 0.33). The obtained phosphors exhibit an excellent light emitting efficiency, color-purity and lower correlated color temperature of the comfortable warm white LEDs.

Keywords: strontium tungstate, phosphors, color-tunable, warm white light emitting diodes.

# **1. INTRODUCTION**

Strontium tungstate (SrWO<sub>4</sub>) has been widely used in optoelectronic industry and solid state laser system because of its interesting physicochemical properties, photocatalytic activity, cathodoluminescence, thermal expansion, and luminescence and so on. Recently, Eu<sup>3+</sup> ions doped SrWO<sub>4</sub> has been intensively researched as a red emitting phosphor for near ultraviolet (UV) and blue lightbased white light emitting diodes (LEDs). They have been received widely attention recently due to their potential applications in catalysts, white LEDs, photoluminescent devices, solar cell, fluorescent lamps and more. Cavalcante et al. studied the Rietveld refinement and optical properties of SrWO<sub>4</sub>:Eu<sup>3+</sup> powders [1]. Hu et al. first observed the red afterglow of  $Eu^{3+}$  in MWO<sub>4</sub> (M = Sr, Ba) matrix [2]. There was an obvious charge imbalance in the lattice when Eu<sup>3+</sup> ions were substituted for Sr<sup>2+</sup> ions, which could affect the luminescence properties. The imbalance problem can be solved by charge compensation [3]. Among the trivalent rare-earth (RE<sup>3+</sup>) ions, Sm<sup>3+</sup> ion is an excellent activator ion. For instance, one-dimensional Sm<sup>3+</sup> doped SrWO<sub>4</sub> with or without different charge compensation approaches (co-doping Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>) orange phosphor have been reported [4]. Sun et al. investigated the formation process and the electron trapping luminescence properties of SrSO<sub>4</sub>:Sm<sup>3+</sup> phosphors [5]. Liu et al. synthesized the reddish orange Sm<sup>3+</sup>-doped BaTiO<sub>3</sub> phosphors for white LEDs [6]. Singh et al. studied the predominant orange red light emission from Sm<sup>3+</sup> doped SrWO<sub>4</sub> phosphors [7].

Energy transfer (ET) from sensitizer to activator could enhance the emission of the activator. The energy can transfer from  $Eu^{3+}$  to  $Sm^{3+}$  in SrWO<sub>4</sub> phosphors [8-10] and maybe it can enhance the photoluminescence (PL) properties of SrWO<sub>4</sub>:Eu<sup>3+</sup> phosphors.

In this work, the SrWO<sub>4</sub>:Eu<sup>3+</sup>, Sm<sup>3+</sup> phosphors were prepared by the simple coprecipitation method in air atmosphere. The phase structure, morphology, PL properties, Commission Internationale de l'Eclairage (CIE) 1931 x-y indexes and color temperature were investigated in detail. Moreover, the ET mechanism was discussed in detail, and the critical distance of ET was calculated. The CIE chromaticity coordinate was also presented.

# 2. EXPERIMENTAL

#### 2.1. Preparation

A series of Sm<sup>3+</sup>-doped Sr<sub>0.80</sub>WO<sub>4</sub>:Eu<sup>3+</sup><sub>0.20</sub> phosphors were obtained by co-precipitation method from sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O) (99.99 % purity, Bailingwei Chemicals Co., Ltd., China), strontium nitrate [Sr(NO<sub>3</sub>)<sub>2</sub>] (98 % purity, Beijing Yili Fina Chenmicals Co., Ltd., China), europium oxide (Eu<sub>2</sub>O<sub>3</sub>) (99.99 % purity, Haweiruike Chemicals Co., Ltd., China), samarium oxide (Sm<sub>2</sub>O<sub>3</sub>) (99.99 % purity, Haweiruike Chemicals Co., Ltd., China), nitric acid (HNO<sub>3</sub>) (analytical grade, Bailingwei Chemical Reagent Co., Ltd., China) and polyethylene glycol ( $[C_4H_{10}O_3]_n$ ) as the starting materials. The molar concentration of the activator  $Sm^{3+}$  was varied from 0.1% to 5%. Firstly, according to Sr<sub>0.80</sub>WO<sub>4</sub>:Eu<sup>3+</sup><sub>0.20</sub>, Sm<sup>+3</sup><sub>x</sub>, stoichiometric composition of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and Sr(NO<sub>3</sub>)<sub>2</sub> were dissolved in deionized water to form the

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aqueous solutions. Then stoichiometric Eu<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub> was dissolved in diluted HNO<sub>3</sub> to offer the Eu<sup>3+</sup> and Sm<sup>3+</sup> ions, respectively. Afterwards mixing both of them together and adding dropwise into the Sr(NO<sub>3</sub>)<sub>2</sub> aqueous solution. The aqueous solution was stirred continuously for 30 min in ultrasound at the room temperature to assure a uniform dispersion. The mixture was dropped to a Na<sub>2</sub>WO<sub>4</sub> solution slowly. The PH of the solution was adjusted to a value within the range of 6 to 7 by addition of aqueous ammonia. The mixed solution was stirred for 60 min at room temperature to form a homogeneous solution.

The resulting precipitate was finally collected by many times centrifugation at 4500 rpm for 20 min and then dried at 80 °C for 2 hours. After that, the mixture was grounded thoroughly in an agate mortar and introduced into a muffle furnace maintained at 700-900 °C for 2 hours. Finally, the dried powders were ground lightly and used for characterization.

## 2.2. Characterizations

The crystal structure was identified by SHIMADZU X-ray diffraction (XRD)-6000 using Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å). The field emission scanning electronic microscopy (FE-SEM) spectrum was measured using Hitachi S-4800. The excitation and emission spectra were recorded at room temperature using a Hitachi F-4500 with a Xe lamp.

## **3. RESULTS AND DISCUSSION**

#### 3.1. Structure and morphology

In order to characterize the crystal phase of the asprepared powder samples, the XRD pattern of the SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>, 0.01Sm<sup>3+</sup> phosphors annealed at 800 °C are presented in Fig. 1. All the strong diffraction peaks can be assigned to the pure tetragonal structure, following Joint Committee on Powder Diffraction Standards Card (JCPDS) No. 85-0587. Its lattice parameters are a = b = 5.416 Å and c = 11.95 Å. It can be considered that Sm<sup>3+</sup> and Eu<sup>3+</sup> have been effectively built into the SrWO<sub>4</sub> host lattice because of no additional peaks of other phases have been observed in the as-obtained samples.



Fig. 1. The XRD pattern of SrWO4:0.20Eu<sup>3+</sup>, 0.01Sm<sup>3+</sup> phosphors and the JCPDS No. 85-0587 database standard for SrWO4

The crystal structure of SrWO<sub>4</sub> is shown in Fig. 2, The SrWO<sub>4</sub> single crystal belongs to tetragonal sheelite structure with  $I4_1/a$  space group. The WO<sub>4</sub><sup>2-</sup> tetrahedral

configuration is built up of hexavalent tungsten ( $W^{6+}$ ) surrounded by four oxygens (O) atoms in this crystal and divalent metal, strontium (Sr), shares corners with eight adjacent O sites, forming a [ $WO_4$ ]<sup>2-</sup> tetrahedron.



Fig. 2. View of the crystal structure of strontium tungstate

SrWO<sub>4</sub> almost remains its main crystal lattice structure when Sr<sup>2+</sup> sites are substituted by other RE<sup>3+</sup> ions. In this distorted dodecahedron geometry, Sr<sup>2+</sup> and RE<sup>3+</sup> atoms are coordinated to eight oxygen atoms considered as [SrO<sub>8</sub>] and [REO<sub>8</sub>] groups. Also, the slight shift of the XRD patterns of SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>, 0.01Sm<sup>3+</sup> relevant to the SrWO<sub>4</sub> host can be observed and attributed to the different radii between Sr<sup>2+</sup> (1.18 Å) and rare earth ions [Sm<sup>3+</sup> (0.96 Å) and Eu<sup>3+</sup> (0.95 Å), which have the similar ionic radius].

The FE-SEM images for the SrWO<sub>4</sub>: $0.20Eu^{3+}$ ,  $0.01Sm^{3+}$  sample are shown Fig. 3. It can be clearly seen that the phosphors consist of large quantities of grains, and the average size of the grains is about 3 µm. From the high magnification SEM, it can be seen the grains is anomalistic but the surface is smooth.



**Fig. 3.** SEM image of SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>,0.01Sm<sup>3+</sup> particles

#### **3.2.** Photoluminescence properties

The excitation (left) and emission (right) spectra of SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>, 0.01Sm<sup>3+</sup> phosphors are presented in Fig. 4. Fig. 4 a shows the excitation (the black line under 613 nm excitation) and emission (the green, pink and red lines under 465 nm, 395 nm and 362 nm excitation, respectively) spectra. The excitation spectrum is found to consist of a broad excitation band at about 220–330 nm and a series of much weaker electronic transitions of Eu<sup>3+</sup> (4f<sup>6</sup>) in the longer wavelength region, which are listed in Table 1. Among these excitation transitions, 395 nm (<sup>5</sup>L<sub>6</sub>), 465 nm (<sup>5</sup>D<sub>2</sub>) and 536 nm (<sup>5</sup>D<sub>1</sub>) lines are the most intense ones, which are assigned as the transitions from the <sup>7</sup>F<sub>0</sub> ground state to the different excited states of Eu<sup>3+</sup>, respectively. In addition, the intensities of the f-f transition

emission for the  $Eu^{3+}$  ions are much higher than that of broadband, indicating that the excitation is mainly through the f-f transition emission of the  $Eu^{3+}$  ions.



**Fig. 4.** The excitation and emission spectra of SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>,0.01Sm<sup>3+</sup> phosphors under various excitation wavelengths. The insets show the enlarge views of diffraction peaks

Table 1. Transition	energies	of	Eu <sup>3+</sup>	ions	in	excit	ation	and
emission	spectra	of	SrW	O4:0.	20E	u <sup>3+</sup> ,	0.015	Sm <sup>3+</sup>
phosphors								

Transitions	Excitation maximum, nm	Transitions	Excitation maximum, nm		
$^{7}F_{0}\rightarrow ^{5}D_{4}$	363ª, 367	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	590		
$^{7}F_{0}\rightarrow ^{5}L_{7}$	377, 382ª, 385	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	613		
$^{7}F_{0}\rightarrow ^{5}L_{6}$	395	${}^{5}D_{0} \rightarrow {}^{7}F_{3}$	652		
$^{7}F_{0}\rightarrow ^{5}D_{3}$	416				
$^{7}F_{0}\rightarrow ^{5}D_{2}$	465				
$^{7}F_{1}\rightarrow ^{5}D_{2}$	474				
$^{7}F_{0}\rightarrow ^{5}D_{1}$	527, 536 <sup>a</sup>				
<sup>a</sup> represents the predominant line in the group.					

The emission spectra could be assigned to the characteristic transitions from the  ${}^{5}D_{0}$  to the  ${}^{7}F_{J}$  (J = 0, 1, 2, 3 and 4). The highest emission peaks are located at 613 nm corresponding to the electric dipole  ${}^{5}D_{0}-{}^{7}F_{2}$  transition of Eu<sup>3+</sup>. The higher ones are located at 590 nm corresponding to the parity allowed magnetic dipole transition of  ${}^{5}D_{0}-{}^{7}F_{1}$  line. Fig. 4 b shows the excitation (the black line under 642 nm excitation) and emission (the green and red lines under 404 nm and 480 nm excitation, respectively) spectra.

The excitation spectrum has a broad excitation band at about 200-310 nm, and it can be attributed to the charge transfer (CT) transition from O<sup>2-</sup>-Sm<sup>3+</sup> and W<sup>6+</sup>-O<sup>2-</sup>, and the intra-configurational f-f transitions of Eu<sup>3+</sup> ions and the 4f–4f transitions of Sm<sup>3+</sup> ions in the longer wavelength region, which are listed in Table 2.

**Table 2.** Transition energies of Sm<sup>3+</sup> ions in excitation and emission spectra of SrWO4:0.20Eu<sup>3+</sup>, 0.01Sm<sup>3+</sup> phosphors

Transitions	Excitation maximum, nm	Transitions	Excitation maximum, nm
${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{K}_{17/2}$	346	${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{5/2}$	560
$^{6}\text{H}_{5/2} \rightarrow ^{4}\text{D}_{15/2}$	362	${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{7/2}$	595
${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{L}_{17/2}$	376	${}^{4}\text{G}_{5/2} \rightarrow {}^{6}\text{H}_{9/2}$	641
${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{K}_{11/2}$	404	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	590
${}^{6}\text{H}_{5/2} \rightarrow {}^{4}\text{P}_{5/2}$	419	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	613
$^{6}\text{H}_{5/2} \rightarrow ^{4}\text{I}_{13/2}$	480	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{3}$	650

The SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>, 0.01Sm<sup>3+</sup> phosphor show not only the characteristic emission of Eu<sup>3+</sup>, i.e., <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub> (the yellow light centered at 590 nm), <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub> (the red band centered at 613 nm) and <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>3</sub> (the red band centered at 650 nm), but also the characteristic emission of Sm<sup>3+</sup>, i.e., <sup>4</sup>G<sub>5/2</sub>→<sup>6</sup>H<sub>5/2</sub>, <sup>4</sup>G<sub>5/2</sub>→<sup>6</sup>H<sub>7/2</sub> and <sup>4</sup>G<sub>5/2</sub>→<sup>6</sup>H<sub>9/2</sub> transitions, as shown in the inset. The highest emission peak is located at 595 nm suggesting that Sm<sup>3+</sup> ion replaces the Sr<sup>2+</sup> ion in SrWO<sub>4</sub> host. The emission intensity of Sm<sup>3+</sup> ion is much stronger than that of Eu<sup>3+</sup> ion.



**Fig. 5.** PL spectra of the SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>,0.01Sm<sup>3+</sup> phosphors annealed at different temperature for 2 h excited at 613 nm, 395 nm and 465 nm, respectively

Fig. 5 exhibits the excitation and emission spectra of SrWO<sub>4</sub>: $0.20Eu^{3+}$ ,  $0.01Sm^{3+}$  phosphors annealed at different temperature (700 °C, 800 °C, and 900 °C) for 2 h excited at 613 nm, 395 nm and 465 nm, respectively.

Similar spectra are shown by  $SrWO_4:0.20Eu^{3+}$ ,  $0.01Sm^{3+}$  particles annealed at different temperature. As can be seen, the intensities are seriously affected by calcination temperature. With the increase of calcination temperature, the intensities of both excitation and emission peaks gradual increase firstly and then slightly decrease. The optimal calcination temperature is about 800 °C. The luminescence intensity increases up to about 3 times as compared to its as-prepared sample.

To study the effect of  $\text{Sm}^{3+}$  dopant concentration on luminescence, the x values in  $\text{SrWO}_4$ :0.20Eu<sup>3+</sup>, xSm<sup>3+</sup> phosphors were varied. Fig. 6 shows the variation of the excitation and emission intensities in respect of the Sm<sup>3+</sup> (x = 0.001 ÷ 0.05) doping concentration.



с

Fig. 6. Room-temperature PL spectra of the SrWO<sub>4</sub>: $0.20Eu^{3+}$ ,  $xSm^{3+}$  powders, where x=0.001, 0.003, 0.005, 0.008, 0. 01, 0.02 and 0.05, under 613 nm, 395 nm and 465 nm excitation, respectively

The wavelength pattern of all samples shows similar spectra in Fig. 5. No new peak site has been observed. The luminescent intensities are changed with the increase of  $Sm^{3+}$  concentration. The peak intensity of Eu<sup>3+</sup> enhances

gradually with increasing in Sm<sup>3+</sup> concentration. The results show that the emission intensity can approach its maximum value for Sm<sup>3+</sup> concentration of 0.01 molar ratio. When x exceeds 0.01 molar, the PL intensities decrease rapidly due to concentration quenching effect. The ET mechanism is related to the critical distance  $(R_c)$ . If  $R_{\rm c}$  has the large critical distance, electric multipole interaction will dominate. Otherwise, the energy exchange interaction is more effective, which is moving from the donor to the receptor [11]. In general, the key of the donor and recipient should be shorter than the distance of 0.5 -0.7 nm for the exchange interaction mechanism [12]. To analyze the mechanism of ET between Eu<sup>3+</sup> and Sm<sup>3+</sup>, which was dominated by the exchange interaction or electric multipole-multipole interaction, the  $R_{\rm c}$  for  $SrWO_4{:}0.20Eu^{\bar{3}+},\ 0.01S\bar{m^{3+}}$  can be calculated by the following equation [13–15]:

$$R_{c} = 2 \left( \frac{\mathcal{N}}{4\pi C_{0} N} \right)^{1/3}, \qquad (1)$$

where *V* and *N* are the volume of unit cell and the number of host cations in the crystal, respectively, and  $C_0$ corresponds to the critical concentration (the total concentration of Eu<sup>3+</sup> and Sm<sup>3+</sup>). Herein, N = 4,  $V = 0.351 \text{ nm}^3$ , and  $C_0$  equals to 0.21. According to the Eq. 1, the R<sub>c</sub> can be calculated to be 0.9277 nm. The value here indicates the electric multipolar interactions are of importance for the ET mechanisms between Sm<sup>3+</sup> and Eu<sup>3+</sup>.

Fig. 7 is the simple energy level scheme for Eu<sup>3+</sup> and Sm<sup>3+</sup>, which is used to better describe the ET processes from Sm<sup>3+</sup> to Eu<sup>3+</sup>. The electrons of Sm<sup>3+</sup> are promoted from the ground state (<sup>6</sup>H<sub>5/2</sub> level) to the excited state (<sup>4</sup>K<sub>11/2</sub> level) under excitation of 404 nm, then relaxing to the metastable excited state (<sup>4</sup>G<sub>5/2</sub> level) by nonradiative (NR) relaxation.<sup>13</sup> At the same time, part of the energy in <sup>4</sup>G<sub>5/2</sub> level of Sm<sup>3+</sup> is also transferred to the <sup>5</sup>D<sub>0</sub> level of Eu<sup>3+</sup> by the resonance. The ET from Sm<sup>3+</sup> to Eu<sup>3+</sup> would hardly happen, which can enhance the emission intensity.



Fig. 7. Schematic diagram of the ET process between  $Sm^{3\scriptscriptstyle +}$  and  $Eu^{3\scriptscriptstyle +}$ 

### 3.3. Calculation of color coordinate of the crystals

As shown in Fig. 8 and Table 3, the CIE chromaticity coordinates for SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>,  $xSm^{3+}$  (x = 0.001 ÷ 0.05) under different excitation wavelengths were calculated using the following [16]:

$$x = \frac{X}{X + Y + Z};$$
(2)

Sample SrWO4:0.20Eu <sup>3+</sup> ,	CIE chromaticity coo	CCT (K) at different excitation wavelength				
nSm <sup>3+</sup>	362 nm	395 nm	465 nm	362 nm	395 nm	465 nm
n = 0.001	(0.490, 0.343) yellowish-pink	(0.634, 0.363) reddish-orange	(0.614, 0.373)	1845	2171	1904
n = 0.003	(0.505, 0.301) pink	(0.635, 0.362) reddish-orange	(0.623, 0.370) reddish-orange	1899	2196	1989
n = 0.005	(0.545, 0.345) reddish-orange	(0.637, 0.361) reddish-orange	(0.671, 0.329) red	1776	2232	3728
n = 0.008	(0.567, 0.350) reddish-orange	(0.640, 0.358) reddish-orange	(0.672, 0.328) red	1835	2318	3797
n = 0.01	(0.618, 0.348) reddish-orange	(0.672, 0.327) red	(0.637, 0.360) reddish-orange	2272	3846	2250
n = 0.02	(0.534, 0.345) yellowish-pink	(0.638, 0.359) reddish-orange	(0.630, 0.366) reddish-orange	1754	2278	2092
n = 0.05	(0.526, 0.345) yellowish-pink	(0.632, 0.365) reddish-orange	(0.615, 0.378)	1749	2123	1870

**Table 3.** The CIE chromaticity coordinates and correlated color temperatures of SrWO4:0.20Eu<sup>3+</sup>, nSm<sup>3+</sup> (n = 0.001  $\div$  0.05) phosphorsunder various excitation wavelengths

$$y = \frac{Y}{X + Y + Z},$$
(3)

where *X*, *Y* and *Z* are the tristimulus values. Those values are given by the equations [17]:

$$X = \int_{\lambda} \overline{\mathbf{x}}(\lambda) P(\lambda) d\lambda; \qquad (4)$$

$$Y = \int_{\lambda} \overline{\mathbf{y}}(\lambda) P(\lambda) d\lambda ; \qquad (5)$$

$$Z = \int_{\lambda} \bar{z}(\lambda) P(\lambda) d\lambda , \qquad (6)$$

where  $\lambda$  is the wavelength of the equivalent monochromatic light.  $\bar{x}(\lambda)$ ,  $\bar{y}(\lambda)$  and  $\bar{z}(\lambda)$  are the color matching functions.  $P(\lambda)$  is the spectral power density.



**Fig. 8.** CIE (x, y) chromaticity diagram for the emission spectra of SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>, nSm<sup>3+</sup> (n = 0.003  $\div$  0.05) phosphor. The blue, yellow and green symbols denote the phosphor under 362 nm, 395 nm and 465 nm excitation, respectively

The blue, yellow and green symbols indicate the position of CIE chromaticity coordinates for SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>,  $xSm^{3+}$  (x = 0.001 ÷ 0.05) under 362 nm, 395 nm and 465 nm

excitation, respectively. A tunable color output in visible region by appropriately changing the ratio of doping rare earth ions concentration, excitation energy or calcination temperature. The emission hue can be varied from pink, yellowish-pink, orange, reddish-orange and eventually to red. These phosphors have higher color saturation than  $Y_2O_2S:Eu^{3+}$  red phosphor. It is worth noting that the chromaticity coordinates (x, y) of SrWO4:  $0.20Eu^{3+}$ , xSm<sup>3+</sup> (x =  $0.005 \div 0.01$ ) phosphors are (0.67, 0.33) for the optimal Sm<sup>3+</sup> doping concentration, which coincide with the NTSC system standard red chromaticity (0.67, 0.33). When x = 0.01 molar, the color purity is calculated to be 99.2 %. These results strongly suggest that the novel red phosphor can be commercially utilized in blue LED-based white LEDs with higher *R*a.

The CCT is used to characterize light sources by the simple formulas as follows [18]:

$$CCT = -437n^3 + 3601n^2 - 6861n + 5514.31$$
(7)

$$n = \frac{x - x_e}{y - y_e},\tag{8}$$

where the  $x_e = 0.3320$  and  $y_e = 0.1858$ . The color coordination and the CCT of phosphors are listed in Table 3. These results reveal that the CIE chromaticity coordinates of SrWO4:0.20Eu<sup>3+</sup>, xSm<sup>3+</sup> (x = 0.005 ÷ 0.01) is (0.67, 0.33) at white light CCT of about 3800 K. From these results, the Sm<sup>3+</sup> activated SrWO4:Eu<sup>3+</sup> can be commercially utilized in blue and near UV warm white LEDs with higher *R*a.

#### 4. CONCLUSIONS

In summary, a series of novel color-tunable  $\text{Sm}^{3+}$  activated  $\text{SrWO}_4:0.20\text{Eu}^{3+}$  phosphors are successfully prepared by the simple co-precipitation method at a low temperature (800 °C). The synthesis, structure, morphology, PL and CCT properties for the  $\text{SrWO}_4:0.20\text{Eu}^{3+}$ ,  $\text{xSm}^{3+}$  (x = 0.001 ÷ 0.05) phosphors was reported. The phosphors can be effectively excited by the light of near UV and blue LED. The optimum  $\text{Sm}^{3+}$  doping concentration for  $\text{SrWO}_4:0.20\text{Eu}^{3+}$ ,  $\text{xSm}^{3+}$  phosphors were 0.01 molar. The investigation results demonstrated that the ET from  $\text{Sm}^{3+}$  to

Eu<sup>3+</sup> arose from electric multipolar interaction with a critical distance of approximately 0.9277 nm. The CIE chromaticity coordinate was also presented. The red emitting SrWO<sub>4</sub>:0.20Eu<sup>3+</sup>, xSm<sup>3+</sup> (x = 0.005 ÷ 0.01) phosphors, which is in coincidence with the NTSC system chromaticity, have high efficiency, high color-purity, and higher color saturation than the commercially available Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> red phosphor. In particular, we can appropriately tune color output by changing the ratio of doping rare earth ions concentration, excitation energy or calcination temperature. The obtained phosphors exhibit a high light emitting efficiency, good color-purity, and low CCT, which may be potentially applicable in comfortable warm white LEDs.

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