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Red phosphor $SrWO_4:Eu^{3+}$ for potential application in white LED

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ABSTRACT

A series of red light emissive phosphors $Sr_{1-x}WO_4:Eu^{3+}_x$ ($x = 0.02–0.10$) and $Sr_{0.84}WO_4:Eu^{3+}_{0.08}$, $M^{+}_{0.08}$ (M = Li, Na, K) were prepared through solid-state reactions, and their luminescent properties were studied. The influences of contents of Eu^{3+} and charge compensators on the luminescent properties were discussed. Both the fluorescent intensities and quantum yields are greatly improved through adding charge compensators. The phosphors can be effectively excited by the light of 394 and 465 nm, and show bright red emissions. The decay curves are well fitted with single exponential decay models. Furthermore, the temperature-dependent luminescence indicates the phosphors exhibit small thermal-quenching properties. So the phosphors are able to be applied to white light-emitting diodes.

1. Introduction

White light-emitting diodes (LEDs) provide great superiorities such as low electric consumption, environment-friendly, high brightness, long lifetime, good reliability, fast response [1,2], and extensively applied in solid-state lightings [3]. A white-light LED with a blue InGaN chip in combination with a yellow phosphor ($YAG:Ce^{3+}$) has been commercially available [4]. However, such a combination exhibits a poor color rendering index (<80) due to the lack of a red light component (above 600 nm) [5]. So, some red phosphors are needed to introduce in this combination [6]. One approach to producing white light is the combination of blue LED with green- and red-emitting phosphor materials [7], the other combination is blue LED with green-, yellow- and red-emitting phosphor materials [8]. Another method to assemble white LEDs is to use red, green and blue light-emitting phosphors coated on a near ultraviolet LED chip to generate white light that will yield high quality LED [9,10]. All these applications require red-emitting phosphors; however, commercially red phosphor for white LEDs used $Y_2O_2S:Eu^{3+}$ shows lower efficiency under near-UV or blue light excitations and instability [11]. Therefore, it is important to research red phosphors can applied to white LEDs.

Eu^{3+} has been extensively studied as an activator ion because of its particular spectral characters and has been used in most commercial red phosphors [12]. Eu^{3+} ions activated tungstates have received considerable attention due to the special properties of WO_4^{2-} group [13–21]. These phosphors show excellent thermal and hydrolytic stability, and have strong absorption in the near ultraviolet region. Therefore, tungstates are good choice as host materials for white LEDs. For all that, little attention has been paid to the luminescent properties of Eu^{3+}-doped $SrWO_4$. So we prepared $SrWO_4:Eu^{3+}$ and studied the luminescent properties. Very recently, we reported a novel phosphor $SrWO_4:Sm^{3+}$ [22]. The phosphor $SrWO_4:Sm^{3+}$ was synthesized by high temperature solid-state reaction in air atmosphere, with same prepared method of $SrWO_4:Eu^{3+}$. In the emission spectrum of $SrWO_4:Sm^{3+}$, three peaks locate at 562 nm, 596 nm and 642 nm, corresponding to CIE chromaticity coordinates of $x = 0.54$ and $y = 0.46$, which indicates the orange light emitting; for $SrWO_4:Eu^{3+}$, the emission spectrum is consist of strong peaks around 612 and 615 nm and weak peaks around 590, 654 and 700 nm, it has CIE chromaticity coordinates of ($x = 0.65$, $y = 0.35$), and shows red light emission. The phosphor $SrWO_4:Sm^{3+}$ can be efficiently excited by ultraviolet; while the excitation bands of $SrWO_4:Eu^{3+}$ are matched well with the characteristic emission from near-UV and blue LED. The temperature-dependent luminescence indicate both the phosphors $SrWO_4:Sm^{3+}$ and $SrWO_4:Eu^{3+}$ exhibit small thermal-quenching properties.

In this paper, the luminescent properties $Sr_{1-x}WO_4:Eu^{3+}_x$ ($x = 0.02–0.10$) and $Sr_{0.84}WO_4:Eu^{3+}_{0.08}$, $M^{+}_{0.08}$ (M = Li, Na, K) were investigated. The chromaticity coordinates were compared with that of commercial red phosphor $Y_2O_2S:Eu^{3+}$, and the results show that the chromaticity coordinates of our phosphors closer to the standard of NTSC ($x = 0.67$, $y = 0.33$) than the commercial red phosphor $Y_2O_2S:Eu^{3+}$. Since the ability to withstand high temperature is

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a basic requirement for phosphor applied in LEDs, the thermally stable properties of the phosphor were investigated, and it turned out to be excellent. So the phosphor is a potential red component for white light-emitting diodes.

2. Experimental

A series of Eu^{3+} doped and Eu^{3+}, M^{+} co-doped $SrWO_4$ phosphors were prepared by solid-state reaction method from $SrCO_3$ (A.R.), WO_3 (A.R.) and Eu_2O_3 (99.99%) as the starting materials [22] using Li_2CO_3 (A.R.), Na_2CO_3 (A.R.) and K_2CO_3 (A.R.) as the other materials. The molar concentration of the activator Eu^{3+} ions varied from 2% to 10%.

The synthesized products were characterized by X-ray diffraction (XRD) using a RigakuD/MAX-2400 X-ray diffractometer. The chromaticity coordinates calculated by the CIE system. Temperature-dependent luminescence of phosphor was measured on a Hitachi F-4500 fluorescence spectrophotometer. More details see reference [22]. Fourier transform infrared spectroscopy (FT-IR) data were collected on a Nicolet 5700 infrared spectrotometer in the range of 400–1500 cm^{-1} using KBr pellets.

The photoluminescent (PL) spectra, fluorescent quantum yield and fluorescent lifetime measurements were carried out on an Edinburgh FLS 920 combined fluorescence lifetime and steady state spectrometer. The FLS 920 spectrometer is equipped with a 450 W xenon lamp for photoluminescent (PL) spectra and an optical parametric oscillator for lifetime measurements. The excitation spectra were obtained scanning from 240 to 480 nm monitored at 615 nm. The emission spectra were scanned from 580 to 710 nm while excited at 394 and 465 nm, respectively. The fluorescent quantum yields were measured using an integrating sphere. Excitaition light source: 450 W xenon lamp; surface coating of the intergating sphere: barium sulfate; data acquiring technology: single photo counting mode; excitation wavelength: 394 and 465 nm, respectively.

All measurements were carried out at room temperature except for the temperature-dependent luminescence.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the standard pattern JCPDS No. 08-0490 and sample $Sr_{1-x}WO_4:Eu_x^{3+}$ ($x = 0.02$–0.10). All the strong peaks of the samples can be assigned to the tetragonal phase $SrWO_4$ ($a = 5.416$ Å and $c = 11.95$ Å) reported in the literature (JCPDS 08-0490).

It can be considered that the as-obtained samples have good crystallinities and no other impurities were observed in the products. The crystal structure of strontium tungstate ($SrWO_4$) is shown in Fig. 2. The strontium tungstate ($SrWO_4$) belongs to sheelite structure [23], and W^{6+} occupies the tetrahedral sites constructed by O^{2-} in this structure; composing WO_4^{2-} anion complex. Sr^{2+} is eight-coordinated by O^{2-}, thus formed a distorted cube. The radius of Sr^{2+} is 1.16 Å (when coordination number CN = 8) and Eu^{3+} is 1.07 Å (when coordination number CN = 8), it is presumed that Sr^{2+} can be occupied by the Eu^{3+} ions.

The FT-IR spectra of the samples provide an accessorial explanation to the products' structures. The FT-IR spectra of $Sr_{1-x}WO_4:Eu_x^{3+}$ with different contents of Eu^{3+} are shown in Fig. 3. Vibration wave numbers (cm^{-1}) and assignments for $Sr_{1-x}WO_4:Eu_x^{3+}$ ($x = 0.02$–0.10) are listed in Table 1.

It can be seen from Fig. 3 that a strong absorption band at 815 cm^{-1} which related to O–W–O stretches of the WO_4 tetrahe-

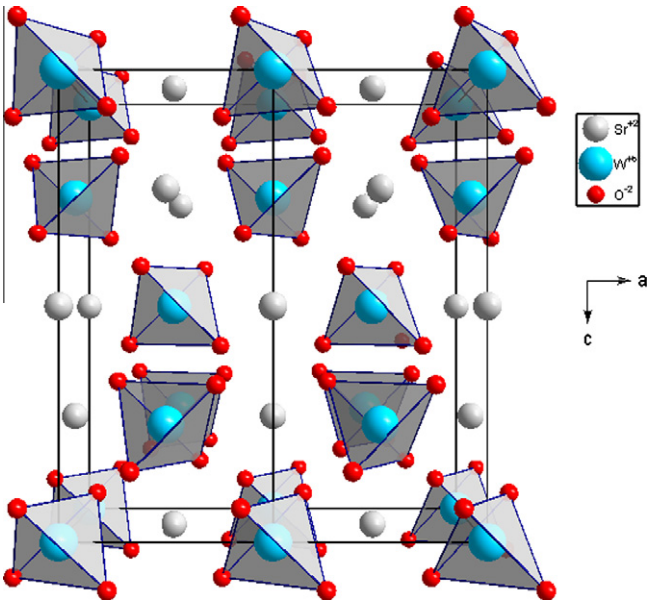

Fig. 2. Crystal structure of $SrWO_4$.

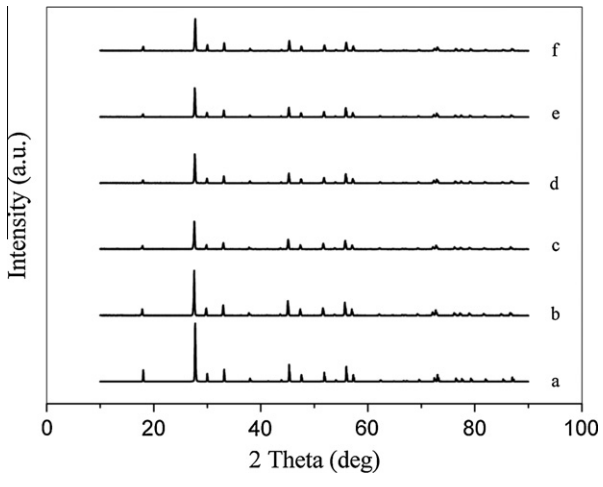

Fig. 1. XRD patterns JCPDS No. 08-0490 database standard for $SrWO_4$ (a) and $Sr_{1-x}WO_4:Eu_x^{3+}$ with different contents of Eu^{3+}: $x = 0.02$ (b); $x = 0.04$ (c); $x = 0.06$ (d); $x = 0.08$ (e), $x = 0.10$ (f).

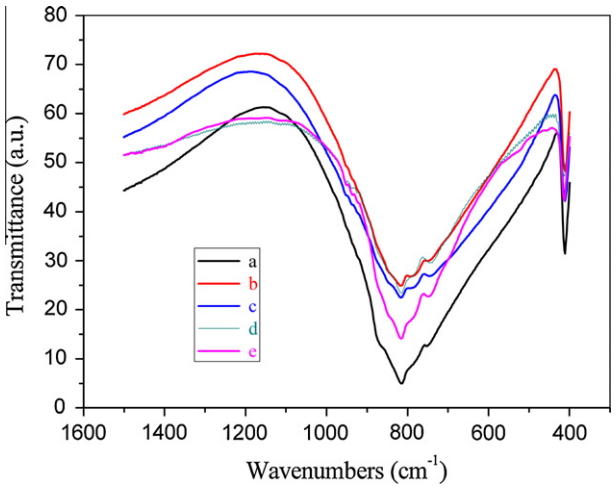

Fig. 3. FT-IR spectra of $Sr_{1-x}WO_4:Eu_x^{3+}$ with different contents of Eu^{3+}: $x = 0.02$ (a); $x = 0.04$ (b); $x = 0.06$ (c); $x = 0.08$ (d); $x = 0.10$ (e).