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A novel orange emissive phosphor $SrWO_4$:Sm^{3+} for white light-emitting diodes

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ABSTRACT

A novel orange emissive phosphor, Sm^{3+}-doped $SrWO_4$, was synthesized by high temperature solid-state reaction in air atmosphere. The excitation spectra show that the phosphors can be efficiently excited by ultraviolet and near-ultraviolet light, the optimized concentration is 4 mol%. Three emission peaks locate at 562, 596 and 642 nm, corresponding to CIE chromaticity coordinates of ($x = 0.54$, $y = 0.46$), which indicates the orange light emitting. The decay curves are well fitted with triple-exponential decay models. The quantum yield of the $Sr_{0.96}Sm_{0.04}WO_4$ phosphor is about 70.65% under excitation of 377 nm. Furthermore, the temperature-dependent luminescence indicates the phosphor exhibits a small thermal-quenching property. So the phosphor is able to be applied to UV-LED chip-based white light-emitting diodes.

1. Introduction

White light-emitting diodes (LEDs) provide great superiorities such as high efficiency, energy-saving, environment-friendly, fast response, long lifetime and good reliability, etc.; thereby they have attracted much attention. Considering energy savings and environmental friendliness, white LEDs are most potential solid-state lighting sources to replace conventional incandescent and fluorescent lamps [1,2]. Therefore, white LEDs are in highly demand especially in the field of solid-state lightings. Since much effect has been devoted to the research of white LEDs, much progress has recently been made. For example, many researches focused on the phosphors used for phosphor-converted white LEDs [3–30], and quantum dots (QDs) have been highlighted as color-converting components in the fabrication of white LEDs [31–33]; some reports directed towards the phosphor-free white LEDs [34,35]. Even so, exploring new materials and technology is still appealing to most of researchers.

There are several ways to gain white light. One of them is the combination of UV-LED with cyan- and orange-emitting phosphor materials. In recent years, some rare-earth ions activated tungstates and molybdates [2,36–44] have been extensively researched because of the special properties of WO_4^{2-} and MoO_4^{2-} group. These phosphors show excellent thermal and hydrolytic stability, and have strong absorption within the ultraviolet region; therefore, tungstates and molybdates are good choice as host materials for white LEDs. Among rare-earth ions, Sm^{3+} ion is well known as an important activator for many different inorganic lattice producing reddish orange light emitting due to its $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2$, 7/2, 9/2, 11/2) transitions. Yang et al. [45] prepared $SrZnO_2$:Sm^{3+} and studied the luminescent properties. Li et al. [46] synthesized Y_2O_2S:Sm^{3+} by combustion method, and investigated its luminescent properties. The luminescent characteristics of $LiCaBO_3$:M (M = Eu, Sm, Tb, Ce, Dy) phosphor for white LED was investigated by Li et al. [47]. For all that, little attention has been paid to the luminescent properties of Sm^{3+}-doped tungstates and molybdates, this motivated us to design and fabricate phosphor $SrWO_4$:Sm^{3+}. Fortunately, we prepared orange light-emitting phosphor $SrWO_4$:Sm^{3+} successfully. The phosphor can be applied to the white LEDs field above mentioned.

In the present work, the luminescent properties of Sm^{3+}-doped $SrWO_4$ were studied, and the influence of the concentration of Sm^{3+} on the luminescent intensity were investigated. The chromaticity coordinates of $x = 0.54$ and $y = 0.46$ have been calculated from the emissional spectra gained by the CIE (Commission International de l'Eclairage, France) system, it does not mean a monochromatic color having a single peak in the spectra but a mixture of three peaks (562, 596 and 642 nm). Since the ability to withstand high temperature is a basic requirement for phosphor applied in LEDs, the thermally stable property of the phosphor was investigated, and it turned out to be excellent. So the phosphor is a potential orange component for white light-emitting diodes that based on UV-LEDs.

2. Experimental

2.1. Samples preparation

The phosphors $Sr_{1-x}Sm_xWO_4$ ($x = 0.02$–0.06) were synthesized by solid-state reaction method. Appropriate amount of $SrCO_3$ (A.R.), WO_3 (A.R.) and Sm_2O_3 (99.9%)

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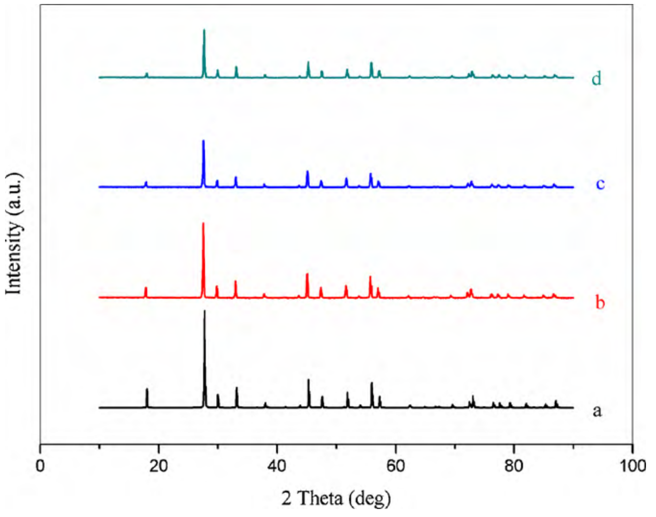

Fig. 1. XRD patterns JCPDS No. 08-0490 database standard for $SrWO_4$ (a) and $Sr_{1-x}Sm_xWO_4$ with different contents of Sm^{3+}: $x = 0.02$ (b); $x = 0.04$ (c); $x = 0.06$ (d).

were thoroughly mixed in an agate mortar and then triturated with distilled ethanol for an ideal mixing. Afterwards, the mixtures were put into alumina crucibles and calcined in a muffle furnace at 1050–1100 °C for 3 h in air, followed by subsequent cooling in air to ambient temperature. The obtained samples were ground lightly into powders and taken to characterization.

2.2. *Characterization*

The synthesized products were characterized by X-ray diffraction (XRD) using a RigakuD/MAX-2400 X-ray diffractometer with Cu $K\alpha$ ($\lambda = 1.5406$ Å) at 40 kV, 60 mA. The XRD patterns were collected in the 2θ range from 10° to 90° with a step of 0.02°. The photoluminescent (PL) spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer equipped with a Xe lamp as the excitation source. The chromaticity coordinates have been calculated from the emissional spectra using the CIE (Commission International de l'Eclairage, France) system.

Fluorescent lifetime and fluorescent quantum yield measurements were carried out on an Edinburgh FLS 920 combined fluorescence lifetime and steady state spectrometer. The FLS 920 spectrometer is equipped with an optical parametric oscillator for lifetime measurement and a 450-W Xenon lamp for quantum yield measurement. The quantum yield was measured by absolute method using an integrating sphere. Firstly, no sample was placed on the sample holder, laser light alone is detected by the spectrometer, and the integral value of this blank was labeled as A. Secondly, the sample was placed on the sample holder and detected by the spectrometer, the integral value of sample of excitation was labeled as B, and the integral value of sample of emission was labeled as C. The quantum yield was calculated with the following formula: $QY = C/(A - B) \times 100\%$.

Temperature-dependent luminescence of phosphor were measured at 20–200 °C using a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp as the excitation source. The powder sample was heated to desired temperatures and kept for 20 min for each temperature point to reach thermal equilibrium. To simply evaluation the temperature dependence, the normalized PL intensity was used which was defined as relative PL intensity (T) = PL intensity (T)/PL intensity (20 °C).

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 $SrWO_4:Sm^{3+}$. 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 strontium tungstate ($SrWO_4$) belongs to sheelite structure [48], 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 1.12 Å, Sm^{3+} 0.96 Å and W^{6+} 0.62 Å, and it can be presumed that the Sm^{3+} ions substitute for the Sr^{2+} sites.

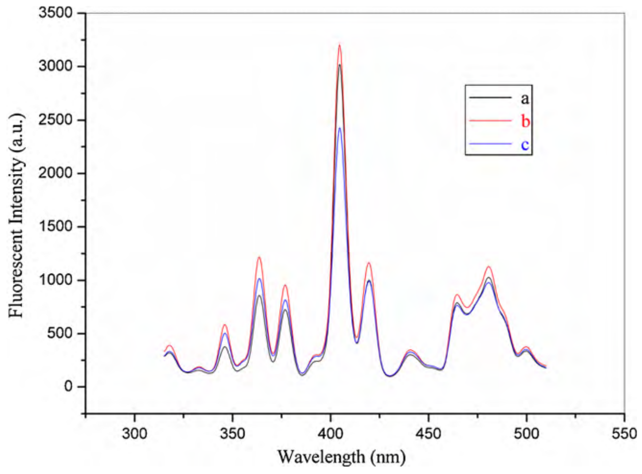

Fig. 2. Excitation spectra of $Sr_{1-x}Sm_xWO_4$ ($\lambda_{em} = 596$ nm) with different contents of Sm^{3+}: $x = 0.02$ (a); $x = 0.04$ (b); $x = 0.06$ (c).

The excitation spectra of $Sr_{1-x}Sm_xWO_4$ ($x = 0.02$–0.06) monitored at 596 nm are shown in Fig. 2. It can be seen from Fig. 2 that the excitation spectra consist of a series of peaks in the range of 315–510 nm. The strongest one at 405 nm and some peaks at 318, 346, 364, 377, 420, 441, 465 and 481 nm are ascribed to the transitions from the ground state to the excited states of Sm^{3+}.

These samples with similar peaks, but the differences of the fluorescent intensity can be clearly observed from Fig. 2. Along with the content increase of Sm^{3+}, the fluorescent intensity also increased, and that reached the highest intensity when the content of Sm^{3+} increased to 0.04. After that, the fluorescent intensity began to decrease.

Fig. 3 shows the emission spectra of $Sr_{1-x}Sm_xWO_4$ ($x = 0.02$–0.06) excited under 364 nm at ambient temperature. It is can be obviously seen that these samples with the same shape and positions, at least three strong peaks located at 562, 596 and 642 nm can be observed, and they can be assigned to the $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2, 7/2, 9/2$) transitions of Sm^{3+} ion [47]. The peak at 596 nm is the strongest one; two secondary peaks exist at 562 and 642 nm, respectively. The luminous colors of the phosphors are orange as result of complex spectra. In general, luminous color is represented by color coordinates and color ratios. At the present work, the values of chromaticity coordinate of the phosphor $Sr_{0.96}Sm_{0.04}WO_4$ has been calculated using the CIE (Commission

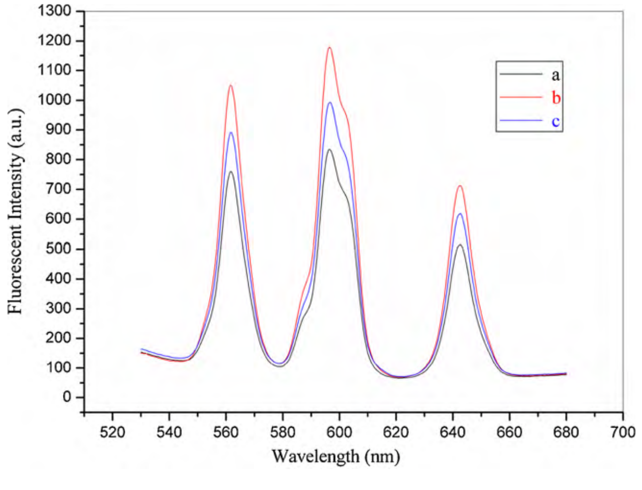

Fig. 3. Emission spectra of $Sr_{1-x}Sm_xWO_4$ ($\lambda_{ex} = 364$ nm) with different contents of Sm^{3+}: $x = 0.02$ (a); $x = 0.04$ (b); $x = 0.06$ (c).

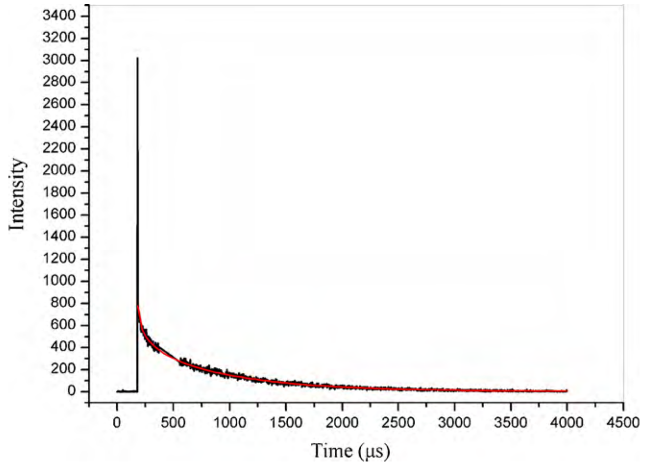

Fig. 4. Fluorescent decay curves of $Sr_{0.96}Sm_{0.04}WO_4$ emission at 596 nm excited by 377 nm (red line shows the fitting result). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

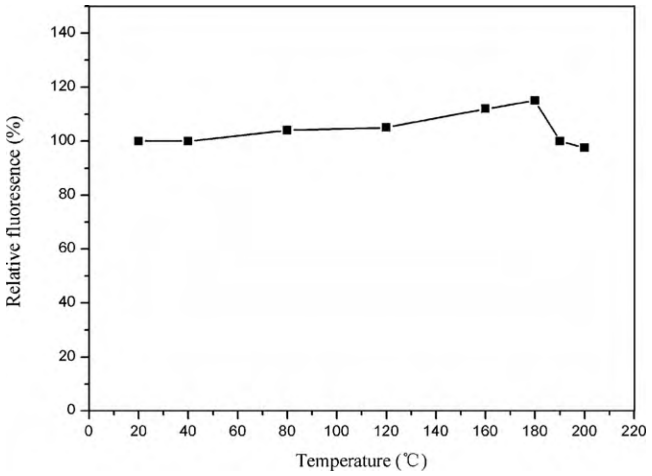

Fig. 5. Temperature-dependent luminescence of $Sr_{0.96}Sm_{0.04}WO_4$ (λ_{ex} = 364 nm).

International de l'Eclairage, France) system. It has been found that the sample has chromaticity coordinates of $x = 0.54$ and $y = 0.46$, which shows orange light emission.

It also can be seen from Fig. 3 that the concentration of Sm^{3+} ions has little affection on the position of emission peaks; but seriously affected the fluorescent intensity. It was quite clear that the fluorescent intensity increase with the increasing concentration of Sm^{3+} ion up to $x = 0.04$, then decreased beyond the concentration due to concentration quenching. The reason lies in that odds of complex of non-radiative transition is increasing as the content of Sm^{3+} is increasing, as a result, the fluorescent intensity of the phosphors becomes lower.

The emission spectra of $Sr_{1-x}Sm_xWO_4$ ($x = 0.02–0.06$) excited by 346 and 377 nm show identical features with that excited by 364 nm, and the optimized concentration is 4 mol%, however, the fluorescent intensity is lower than that under 364 nm excitation. The result indicates that the phosphor can be more effectively excited by ultraviolet 364 nm light. The chromaticity coordinates of the phosphor $Sr_{0.96}Sm_{0.04}WO_4$ have been calculated from the emissional spectra (λ_{ex} = 377 nm) using the CIE system, it has chromaticity coordinates of $x = 0.54$ and $y = 0.46$, which also shows orange light emission.

At room temperature, for phosphor $Sr_{0.96}Sm_{0.04}WO_4$, the fluorescent decay curves corresponding to the emissional line at 562, 596 and 642 nm of the Sm^{3+} ion with identical features (λ_{ex} = 377 nm). As an instance, the fluorescent decay curve of $Sr_{0.96}Sm_{0.04}WO_4$ for 596 nm emission and fitting curve are shown in Fig. 4. The decay behavior can be expressed as follows:

$$I = I_0 + A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) + A_3 \exp\left(\frac{-t}{\tau_3}\right)$$

where I and I_0 are phosphorescence intensity, A_1, A_2 and A_3 are constants and t is time: τ_1, τ_2 and τ_3 are decay time for exponential components, respectively. They are well fitted with triple-exponential function, and the fluorescent lifetimes of the sample emitted at 562 nm is measured to be $\tau_1 = 0.0035$ ms, $\tau_2 = 0.11$ ms and $\tau_3 = 0.75$ ms. The values of fluorescent lifetime emitted at 596 nm are $\tau_1 = 0.0031$ ms, $\tau_2 = 0.097$ ms and $\tau_3 = 0.75$ ms; the data of fluorescent lifetime emitted at 642 nm are $\tau_1 = 0.0037$ ms, $\tau_2 = 0.096$ ms and $\tau_3 = 0.74$ ms, respectively.

The thermal-quenching property is an important technological parameter for phosphors applied in white LEDs [49], especially in high-power white LED devices. The thermal-quenching properties of the phosphor $Sr_{0.96}Sm_{0.04}WO_4$ were investigated in the temperature range from 20 to 200 °C. The obtained results are presented in Fig. 5. It can be seen that the phosphor shows unusual thermal-quenching behavior. The fluorescent intensity increased as the temperature was elevated. At a certain temperature (180 °C), the fluorescent intensity approached to a maximum, and the decrease as the temperature increased continuously. At 190 °C, the fluorescent intensity still maintains about 100% of that measured at the temperature of 20 °C. Although the reasons need further study, nevertheless, the results indicating that the phosphor $SrWO_4:Sm^{3+}$ has a small thermal-quenching property and good suitability for application in white LEDs.

The quantum yield of $Sr_{0.96}Sm_{0.04}WO_4$ is 70.65% when the phosphor under excitation of 377 nm. The result indicates that the phosphor can be effectively excited by ultraviolet light.

4. Conclusions

In summary, a series of phosphors $Sr_{1-x}Sm_xWO_4$ ($x = 0.02–0.06$) were prepared by solid-state method. The fluorescent intensities of the phosphors excited by 364, 377 and 346 nm reach a maximum at $x = 4$ mol%. The results of fitting the experimental data of fluorescent decay curves revealed that Sm^{3+}-doped $SrWO_4$ phosphor in terms of a triple-exponential decay model. The fluorescent lifetimes of the phosphor emitted at 562, 596 and 642 nm is closer. The quantum yield of the phosphor $Sr_{0.96}Sm_{0.04}WO_4$ is about 70.65% under excitation of 377 nm. In addition, the phosphor shows a small thermal quenching, at 190 °C, the fluorescent intensity still maintains about 100% of that measured at the temperature of 20 °C. Given good overall luminescent performances, this phosphor is a potential candidate as orange-emitting component for white LED.

Acknowledgements

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