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Preparation and luminescence properties of $Sr_7Zr(PO_4)_6:Dy^{3+}$ single-phase full-color phosphor

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Abstract Novel single-phase white-light-emitting $Sr_7Zr(PO_4)_6:Dy^{3+}$ phosphors for light-emitting diode (LED) applications were synthesized by conventional solid-state reactions. The phases and luminescent properties of the obtained $Sr_7Zr(PO_4)_6:Dy^{3+}$ phosphors were characterized. The results show that the luminescence spectra excited by 350 nm consist of two characteristic blue and yellow bands, corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+}, respectively. When $x > 0.02$, the concentration quenching effect occurred, and the critical transfer distance (R_c) was ~19.247 Å. The energy transfer of the Dy^{3+} ions is the electric dipole–dipole interaction mechanism. The International Commission on Illumination chromaticity coordinates for $Sr_{7-x}Zr(PO_4)_6:xDy^{3+}$ phosphors were located in the white region. The developed phosphor has great potential as a single-component white-light-emitting phosphor for UV-LEDs.

1 Introduction

Nowadays, single-phase full-color phosphors are being developed as photoluminescence phosphors for white-light-emitting diodes (w-LEDs) [1–5]. Trivalent dysprosium ion (Dy^{3+})-doped phosphors exhibit intense blue (484 nm) and yellow (575 nm) emissions and generate white-light emission; thus, Dy^{3+}-doped phosphors have been developed as single-phase full-color phosphors [6]. Recently, Dy^{3+}-doped phosphors have been extensively elucidated and investigated for many hosts such as phosphates [7–11], tungstate [12], vanadates [13], molybdates [14], niobate [15], silicates [16–18], aluminates [19], and borates [20–22]. Among these hosts, phosphates have attracted much interest for pc-LEDs because of their excellent thermal luminescence stability arising from a rigid network of PO_4 tetrahedrons. Dy^{3+}-doped phosphors such as $LiSrPO_4$ [7], $NaGd(PO_3)_4$ [8], $Ca_8MgBi(PO_4)_7$ [9], and $NaCaPO_4$ [10] have been recognized as potential white-light-emitting phosphors for near-UV (NUV)-pumped LED applications.

$Sr_7Zr(PO_4)_6$ belongs to a family of eulytite compounds, exhibiting a cubic structure with the space group of $I\bar{4}3d$ ($Z = 2$) [23]. Previously, we reported the preparation and luminescence properties of high-efficiency red-emitting $Sr_7Zr(PO_4)_6:Eu^{3+}$ phosphors, indicating that $Sr_7Zr(PO_4)_6$ is an excellent host for rare-earth ions for doping [24]. The spectral characteristic of Dy^{3+} and crystallographic structure of $Sr_7Zr(PO_4)_6$, inspired us to study the luminescence properties of Dy^{3+}-activated $Sr_7Zr(PO_4)_6$, aiming to investigate the white-light emission of Dy^{3+} under NUV excitation for LED applications.

2 Experimental

$Sr_7Zr(PO_4)_6$ and $Sr_{7-x}Zr(PO_4)_6:xDy^{3+}$ ($x = 0.01$, 0.02, 0.03, 0.04, 0.06, and 0.08) phosphors were synthesized using a solid-state reaction. Highly pure $Sr(NO_3)_2$ (99.9 %), $(NH_4)_2HPO_4$ (99.9 %), ZrO_2 (99.9 %), and Dy_2O_3 (99.99 %) were purchased from Sinopharm Chemical Reagent, Co. Ltd., Shanghai, China, and used as the starting materials. Stoichiometric amounts of these

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reagents were mixed thoroughly in alcohol by ball milling in an agate mortar. They were presintered at 750 °C for 3 h in air and resintered at 1250 °C for 4 h. Finally, the samples were ground into powder for characterization. The phase purities were analyzed using a D/MAX2500TC powder diffractometer. The excitation and emission spectra were measured using a Hitachi F4500 fluorescence spectrophotometer, and the luminescence decay times were measured using a steady-state and transient-state fluorescence spectrometer (FLS920).

3 Results and discussion

3.1 XRD analysis

Figure 1 shows the X-ray diffraction (XRD) patterns of $Sr_7Zr(PO_4)_6$ and $Sr_{7-x}Zr(PO_4)_6{:}xDy^{3+}$ ($x = 0.01$, 0.02, 0.03, 0.04, 0.06, and 0.08) powders. All the observed diffraction peaks can be indexed to the standard data of $Sr_7Zr(PO_4)_6$ with JCPDS card no. 34-0065 [24]. No obvious impurity phase was detected when Dy^{3+} ions were doped into the host lattice.

3.2 Luminescence properties for $Sr_{7-x}Zr(PO_4)_6{:}xDy^{3+}$ phosphors

The excitation and emission spectra of $Sr_{7-x}Zr(PO_4)_6{:}xDy^{3+}$ ($x = 0.01$, 0.02, 0.03, 0.04, 0.06, and 0.08) particles are shown in Fig. 2a and b, respectively. All these spectra exhibited similar shapes for all the as-prepared samples. The excitation bands centered at wavelengths of 324 nm ($^6H_{15/2} \rightarrow {}^4M_{17/2}$), 350 nm ($^6H_{15/2} \rightarrow {}^4M_{15/2}$, $^6P_{7/2}$), 366 nm ($^6H_{15/2} \rightarrow {}^4I_{11/2}$), 387 nm ($^6H_{15/2} \rightarrow {}^4I_{13/2}$, $^4F_{7/2}$),

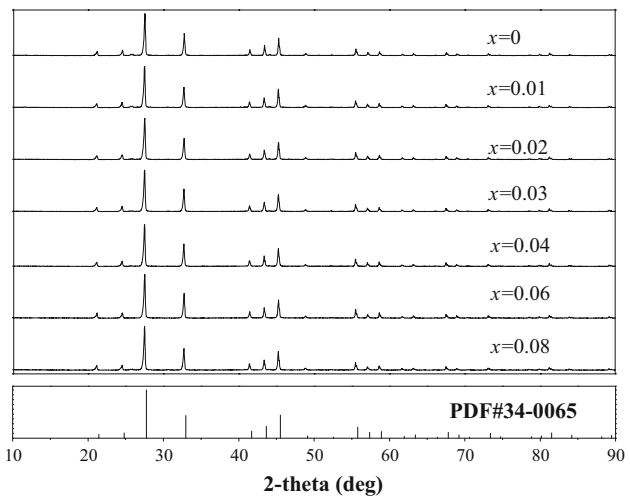

Fig. 1 XRD patterns of the as-prepared samples and vertical lined are correspondent to JCPD#PDF card No. 34-0065

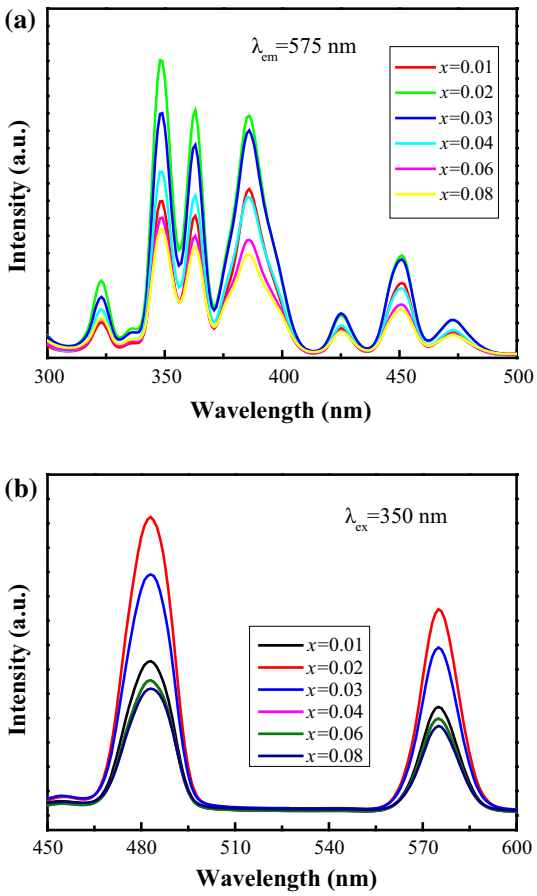

Fig. 2 **a** PLE spectra; **b** PL spectra of $Sr_{7-x}Zr(PO_4)_6{:}xDy^{3+}$ phosphors

427 nm ($^6H_{15/2} \rightarrow {}^4G_{11/2}$), and 448 nm ($^6H_{15/2} \rightarrow {}^4I_{15/2}$) were observed by monitoring at the 572 nm emission of Dy^{3+} ions. The excitation bands of all these phosphors matched well with those of the NUV-emitting In-GaN chip, indicating that they can be used in NUV-pumped w-LEDs. On excitation at 350 nm, the emission transition of Dy^{3+} ions consisted of double emission bands (Fig. 2b). These emission bands can be assigned to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (480 nm) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (572 nm) emissions of Dy^{3+} ions, respectively. Consequently, white-light emission could be achieved with a color mixture of blue (480 nm) and yellow (572 nm) light [6–10].

Figure 3 shows the relative emission intensity as a function of Dy^{3+} concentration x. For $Sr_{7-x}Zr(PO_4)_6{:}xDy^{3+}$, the intensity first increased with increasing Dy^{3+} concentration of up to $x = 0.02$ and then decreased. The photoluminescence (PL) intensity decreased with a concentration of doped Dy^{3+} greater than $x = 0.02$, which can be attributed to the well-known concentration quenching effect.

The critical distance of energy transfer R_c was calculated using the concentration quenching method where the

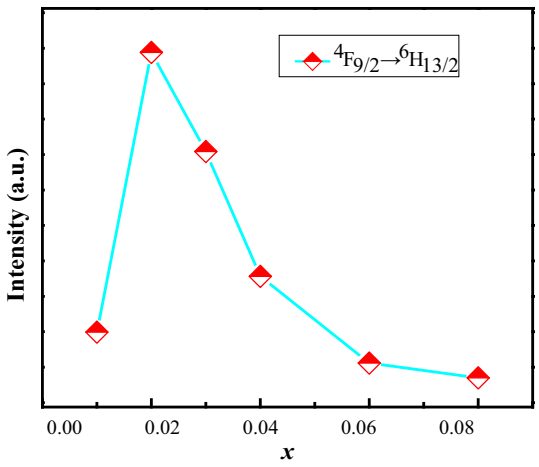

Fig. 3 Relationship between the relative intensity of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition and concentration of Dy^{3+} ions

critical distance between Dy^{3+} ions can be estimated using the following formula suggested by Blasse [25]:

$$R_c = 2\left(\frac{3V}{4\pi N x_c}\right)^{1/3} \quad (1)$$

where x_c is the critical concentration, N is the number of cations in the unit cell, and V the volume of the unit cell ($N = 14$ and $V = 1045.369$ Å^3 for $Sr_7Zr(PO_4)_6$). R_c was calculated to be ~ 19.247 Å.

3.3 The mechanism of the energy transfer among Dy^{3+} ions

According to Huang's rule [24], the relationship between the integral luminescent intensity I and doping concentration x can be expressed as follows:

$$I \propto \alpha^{\left(1-\frac{s}{d}\right)} \Gamma\left(1+\frac{s}{d}\right) \quad (2)$$

$$\alpha = x\Gamma\left(1-\frac{d}{s}\right)\left[X_0\frac{1+A}{\gamma}\right]^{\frac{d}{s}} \quad (3)$$

where γ is the intrinsic transition probability of sensitizer, s is index of electric multipole, which is six, eight and ten for electric dipole–dipole, electric dipole–quadrupole, and electric quadrupole–quadrupole interaction, respectively. If $s = 3$, the interaction type is an exchange interaction. d is the dimension of the sample, here $d = 3$. A and X_0 are the constants and $\Gamma(1 + s/d)$ is a function. From Eqs. (2) and (3), it can be derived that

$$\log\left(\frac{I}{x}\right) = -\frac{s}{d}\log x + \log f \quad (4)$$

where f is independent of the doping concentration. Figure 4 shows the Log(I/x)–Log$x$ plot for the $^4F_{9/2}$

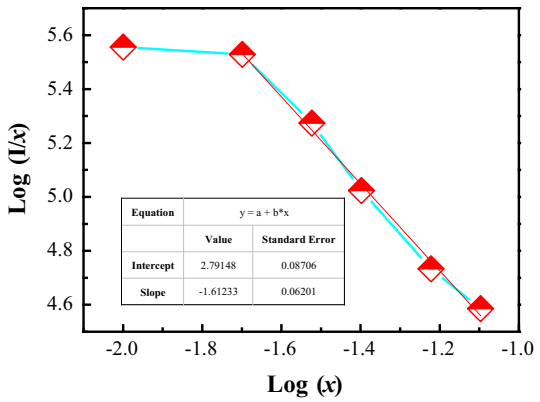

Fig. 4 The relation of the concentration of Dy^{3+} ions Log (x) and the Log(I/x) for the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition by 350 nm light

$\rightarrow {}^6H_{15/2}$ transitions of Dy^{3+} ions in $Sr_{7-x}Zr(PO_4)_6{:}xDy^{3+}$ phosphors. According to (4), using linear fitting to deal with the experimental data in the region of high concentrations, the value of the slope parameter $-s/d$ is obtained to be -1.61 for the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition. The slope parameter is approximately to -2. Therefore, the index of the electric multipole energy transfer is 6. The result means that the electric dipole–dipole interaction mechanism is dominant by the energy transfer of the Dy^{3+} ions in the investigated phosphors.

3.4 Decay curves of Dy^{3+} emission for the as-prepared samples

The decay curves of the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} ions in $Sr_{7-x}Zr(PO_4)_6{:}xDy^{3+}$ ($x = 0.01$, 0.02, 0.03, and 0.04) phosphors were measured, and the results are shown in Fig. 5. The corresponding luminescence decay times can be calculated by the double-exponential decay mode using the following equation [26]:

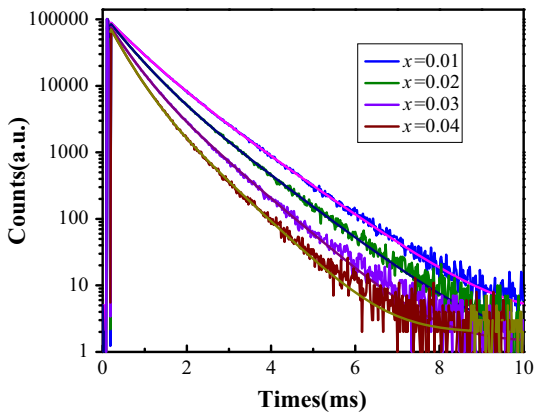

Fig. 5 Decay curves of Dy^{3+} emission for the as-prepared samples

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (5)$$

where I is the luminescence intensity, A_1 and A_2 are the weight constants, t is the time, and τ_1 and τ_2 are the short and long lifetimes of the exponential components, respectively. Then, based on the above parameters, the average decay times (t) can be determined using the following formula [26]:

$$\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (6)$$

After the calculation and analysis, the average decay times (τ^*) are 0.862, 0.765, 0.652, and 0.561 ms for $x = 0.01$, 0.02, 0.03, and 0.04, respectively. The decay times are short enough for using the phosphors in w-LEDs.

3.5 CIE chromaticity coordinates analysis

The International Commission on Illumination (CIE) chromaticity coordinates of $Sr_{7-x}Zr(PO_4)_6$:xDy^{3+} phosphors are shown in Fig. 6. The symbol * in CIE-1931 chromaticity diagram (Fig. 6) shows the ideal white-light chromaticity coordinates with $x = 0.333$ and $y = 0.333$. For $Sr_{7-x}Zr(PO_4)_6$:xDy^{3+}, the CIE values of the phosphors ($x = 0.01$, 0.02, 0.03, 0.04, 0.06, and 0.08) were ($x = 0.261$, $y = 0.264$), ($x = 0.266$, $y = 0.279$), ($x = 0.266$, $y = 0.291$), ($x = 0.269$, $y = 0.303$), ($x = 0.273$, $y = 0.303$), and ($x = 0.261$, $y = 0.275$), respectively. The CIE chromaticity coordinates of these phosphors are located in the white region. The inset of Fig. 6 shows the luminescence photographs of $Sr_{6.98}Zr(PO_4)_6$:$0.02Dy^{3+}$ phosphor excited at 365 nm. This indicates that $Sr_{6.98}Zr(PO_4)_6$:$0.02Dy^{3+}$ phosphor emitted a bright white light.

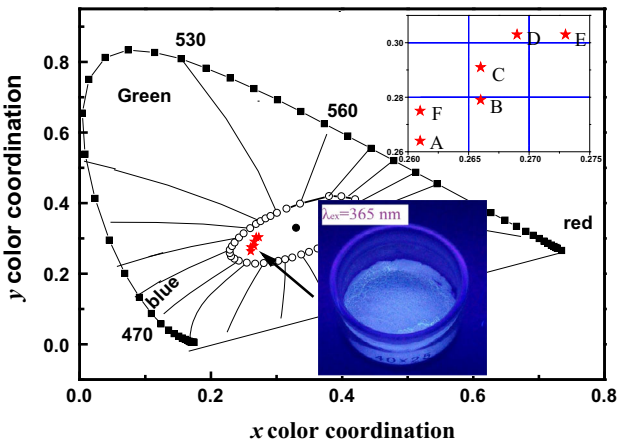

Fig. 6 CIE chromaticity coordinates of the as-prepared samples, the *inset* shows the luminescence photographs of $Sr_{6.98}Zr(PO_4)_6$:$0.02Dy^{3+}$ phosphor excited at 365 nm

4 Conclusions

In summary, $Sr_{7-x}Zr(PO_4)_6$:xDy^{3+} ($x = 0.01$, 0.02, 0.03, 0.04, 0.06, and 0.08) single-phase full-color phosphors were synthesized by a solid-state reaction. The phase analysis, luminescence properties, decay times, and CIE coordinates of the emission were investigated. These phosphors showed double emissions at 480 nm (blue) and 572 nm (yellow) under NUV light excitation. For $Sr_{7-x}Zr(PO_4)_6$:xDy^{3+}, the intensity first increased with increasing Dy^{3+} concentration of up to $x = 0.02$ and then decreased due to the concentration quenching effect. The critical energy transfer distance was ~19.247 Å. The energy transfer of the Dy^{3+} ions in $Sr_{7-x}Zr(PO_4)_6$:xDy^{3+} phosphors is the electric dipole–dipole interaction mechanism. The CIE chromaticity coordinates of $Sr_{7-x}Zr(PO_4)_6$:xDy^{3+} phosphors were located in the white region. These results indicate that $Sr_{7-x}Zr(PO_4)_6$:xDy^{3+} single-phase full-color phosphor has great potential in NUV-emitting w-LED applications, free of complex phosphor blending operations.

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