

Luminescence properties of a novel single-phase white-emitting phosphor based on Dy³⁺ doped strontium tetrphosphate

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Abstract A series of novel single-phase white-emitting phosphors based on Dy³⁺ doped strontium tetrphosphate (Sr₃P₄O₁₃:Dy³⁺) have been synthesized successfully via a conventional solid-state reaction at high temperature, and characterized by X-ray diffraction, photoluminescence excitation/emission spectra and decay curves. The optimum doping concentration of Dy³⁺ in Sr₃P₄O₁₃ was ascertained by investigating the influence of the doping concentration of Dy³⁺ on the emission intensity of Dy³⁺, in which the content of Dy³⁺ did not change the shape and position of emission spectra except for emission intensity. Meanwhile, the critical distance and concentration quenching mechanism were also calculated and confirmed. Furthermore, the decay time was also determined for Sr₃P₄O₁₃:Dy³⁺ phosphors with various concentrations of Dy³⁺, and decreases gradually with increasing Dy³⁺ concentration. The as-prepared Sr₃P₄O₁₃:Dy³⁺ phosphors could be excited by near ultraviolet, and exhibit white-light emission with short decay time of milliseconds, indicating these phosphors could exhibit certain potential as single-phase white-light-emitting phosphors for application in display and lighting regions (e.g. white light-emitting diodes).

1 Introduction

Phosphates are a large family of compounds, which have been utilized widely as host materials of phosphors for many years due to their excellences including low material cost, easy synthesis, good thermal stabilities, and low sintering temperatures [1]. A type of alkaline earth tetrphosphate, Sr₃P₄O₁₃, is an important host material for luminescent activated ions. The crystal structure of Sr₃P₄O₁₃ has been reported by Zhang et al. in 2004 [2]. The host compound crystallizes in triclinic system and builds up from SrO₇ polyhedra and P₄O₁₃⁶⁻ anions. It has a layered structure, in which the Sr atoms are located in the interlayer space. Over the past years, some research groups have given considerable attention to the luminescence properties of Sr₃P₄O₁₃-based phosphors for potential application in display and lighting regions. Cao et al. [3] investigated the photoluminescence properties and energy transfer process of novel red phosphor Sr₃P₄O₁₃:Eu³⁺, Bi³⁺; Zhang et al. [4] investigated the temperature-dependent luminescence properties of Sr₃P₄O₁₃:Eu²⁺ polycrystalline ceramics; Liu et al. [5] investigated the self-reduction process of Eu³⁺ to Eu²⁺ in Sr₃P₄O₁₃ host; Cao et al. [6] developed a novel red phosphor Sr₃P₄O₁₃:Bi²⁺. The above results obtained by these researchers indicated the as-prepared phosphors could be potential candidate phosphors for white light emitting diodes (w-LEDs) based on the near UV and/or blue chips. So, the investigation in-depth on the novel Sr₃P₄O₁₃ based phosphors was indispensable to develop the novel phosphors for possible industrial application. Herein, the phosphate compound strontium tetrphosphate (Sr₃P₄O₁₃) was chose to be the host compound in this work.

Dy³⁺ ion, an important rare earth ion, has been followed enough with interest by researchers in the past years due to

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its characteristic of producing white light in a single host by the combination of its ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (~ 480 nm, blue light) and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm, yellow light) transitions, which has been a research hotspot in order to develop the novel single-phase white-emitting phosphor for possible potential application in w-LEDs [7–16]. As per our knowledge, until now, there were no reports found on the luminescent properties of Dy^{3+} ions activated $\text{Sr}_3\text{P}_4\text{O}_{13}$ host lattice. It is well known that the luminescence properties of phosphor depend on its synthesis process [17]. High-temperature solid-state reaction method is a traditional synthetic method for phosphor. Although this method has its inherent disadvantages [18], such as high reaction temperature and long heating time, up to now, it still has been most commonly used method by many researchers due to the low cost, mass production, and simple preparation process. So, in the current work, Dy^{3+} doped $\text{Sr}_3\text{P}_4\text{O}_{13}$ phosphors were synthesized by an high-temperature solid-state reaction and their photo-luminescent properties were investigated in detail for the first time.

2 Experimental

$\text{Sr}_{3(1-x)}\text{Dy}_{3x}\text{P}_4\text{O}_{13}$ phosphors ($x = 0.005, 0.01, 0.02, 0.03, 0.05$, and 0.1) were synthesized by a conventional solid-state reaction method at high temperature. A stoichiometric amount of the starting materials including SrCO_3 (A.R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R.) and Dy_2O_3 (99.99 % purity) were firstly thoroughly mixed in an agate mortar via a grinding process for half an hour at least. Then the homogeneous mixture was put into a corundum crucible and heated at 900°C for 6 h. Finally, the sample was naturally cooled to room temperature, and crushed into fine particles for the further characterization.

The phase purity of the as-prepared samples was characterized by a powder X-ray diffraction (XRD) analysis with $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation on a Bruker D8 Advance X-Ray Diffractometer. Photoluminescence (PL) spectra and decay curves were measured by using an FLS980-Combined Fluorescence Lifetime and Steady State Fluorescence Spectrometer (EDINBURGH INSTRUMENTS), in which a 450 w xenon lamp and a 100 w $\mu\text{F}2$ microsecond flash lamp were used as the excitation source, respectively. All the above measurements were performed at room temperature.

3 Results and discussion

Figure 1 shows the XRD patterns of $\text{Sr}_{3(1-x)}\text{Dy}_{3x}\text{P}_4\text{O}_{13}$ samples with $x = 0.005, 0.01, 0.02, 0.03, 0.05$ and 0.1 . It is found that all the diffraction peaks agree with the standard

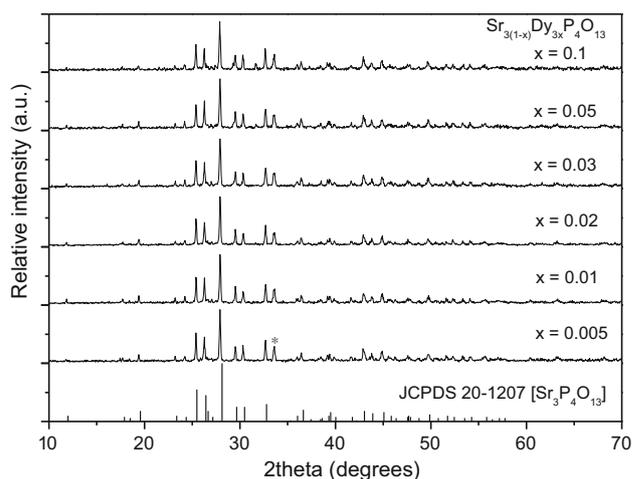


Fig. 1 XRD patterns of $\text{Sr}_{3(1-x)}\text{Dy}_{3x}\text{P}_4\text{O}_{13}$ samples with $x = 0.005, 0.01, 0.02, 0.03, 0.05$ and 0.1

diffraction lines from the Joint Committee on Powder Diffraction Standards (JCPDS) data 20–1207 [$\text{Sr}_3\text{P}_4\text{O}_{13}$] except for a minor peak (marked with*) at $2\theta = 33.6^\circ$. The weak peak in fact can also be attributed to the $\text{Sr}_3\text{P}_4\text{O}_{13}$ host after carefully comparing with the published work about other rare earth ions (Eu^{3+} , Eu^{2+}) doped $\text{Sr}_3\text{P}_4\text{O}_{13}$ and the calculated diffraction lines in term of the crystal structure data of $\text{Sr}_3\text{P}_4\text{O}_{13}$ [4, 5]. In addition, no other impurities or phases are obviously observed, which indicates that the doping of Dy^{3+} ions does not cause significant changes of $\text{Sr}_3\text{P}_4\text{O}_{13}$ crystal structure. Namely, all as-prepared samples are pure single-phase.

Figure 2 shows the emission spectra of $\text{Sr}_{3(1-x)}\text{Dy}_{3x}\text{P}_4\text{O}_{13}$ ($x = 0.005, 0.01, 0.02, 0.03, 0.05$ and 0.1) phosphors upon excitation with 349 nm, which are similar with each other in shape and position except for emission intensity.

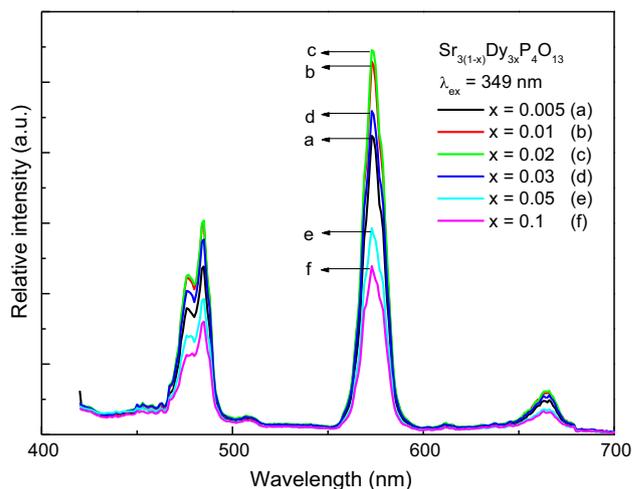


Fig. 2 Emission spectra of $\text{Sr}_{3(1-x)}\text{Dy}_{3x}\text{P}_4\text{O}_{13}$ ($x = 0.005, 0.01, 0.02, 0.03, 0.05$ and 0.1) phosphors upon excitation with 349 nm

These emission spectra show three main emission bands peaking at about 485 nm (blue), 573 nm (yellow), and 663 nm (red), which are attributed to the electronic transitions of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ of Dy^{3+} , respectively [7, 8]. Obviously, the emission intensity of the yellow emission at 573 nm is greater than that of the blue emission at 485 nm, indicating that the local environment around Dy^{3+} ions lacks inversion symmetry in $Sr_3P_4O_{13}$ host lattice [19]. It is also observed that the optimum doping concentration of Dy^{3+} is about 0.02 (x value), and after that the emission intensity decrease with further increase of Dy^{3+} doping concentration due to the concentration quenching phenomenon [10, 19].

Generally speaking, the concentration quenching phenomenon of Dy^{3+} ions is often caused by the non-radiative energy transfer process among Dy^{3+} ions, which may take place via exchange interaction or electric multipolar interaction [7, 11]. The authentic type of interaction for the concentration quenching of Dy^{3+} ions could be ascertained by obtaining the value of the critical distance (R_c) between the nearest Dy^{3+} ions, at which the probability of the nonradiative transfer is equal to the probability of the radiative emission [20]. When the critical distance is shorter than 5 Å, the exchange interaction is predominant interaction mechanism; conversely, the electric multipole interaction is predominant. Thus, the R_c can be estimated from the following formula provided by Blasse [20],

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

where V is the volume of the unit cell, x_c is the critical concentration of activator ion, and N is the number of formula units per unit cell. According to the crystal structure of the $Sr_3P_4O_{13}$ compound [2], $V = 537.757 \text{ \AA}^3$, $N = 2$ and $x_c = 0.02$ for Dy^{3+} . Therefore, R_c was calculated to be about 29.5 Å, which suggests that the multipole interaction is the major mechanism for the concentration quenching of Dy^{3+} in the $Sr_3P_4O_{13}:Dy^{3+}$ phosphors.

As the multipole interaction include three different types: dipole–dipole (d–d), dipole–quadrupole (d–q), quadrupole–quadrupole (q–q) interactions, so the exact type of interaction need to be confirmed further. Fortunately, this matter could be solved by investigating the emission intensity (I) per activator ion concentration (x) in terms of the following equation [21, 22]

$$\frac{I}{x} = \frac{k}{1 + \beta(x)^{\theta/3}} \quad (2)$$

where k and β are constants for each interaction for a given host lattice and $\theta = 6, 8,$ and 10 for d–d, d–q, and q–q interactions, respectively. The above mentioned equation can be rearranged further for $\beta(x)^{\theta/3} \gg 1$ as follows

$$\lg\left(\frac{I}{x}\right) = K' - \frac{\theta}{3}\lg(x) \quad (3)$$

where $K' = \lg K - \lg \beta$. Since the critical concentration of Dy^{3+} has been determined as 0.02, the dependence of the emission intensity of the $Sr_3P_4O_{13}:Dy^{3+}$ phosphors excited at 349 nm on the doped- Dy^{3+} concentration which is not less than the critical concentration (0.02) is determined, which is shown in Fig. 3. The dependence of $\lg(I/x)$ on $\lg(x)$ is found to be relatively linear and the slope ($-\theta/3$) is determined to be -1.54 . Then the value of θ could be calculated to be 4.62, which is close to the value of d–d interaction relative to that of other interactions, which means the d–d interaction is the main mechanism for the concentration quenching of Dy^{3+} in the $Sr_3P_4O_{13}$ host. As the luminescence properties of Dy^{3+} in $Sr_3P_4O_{13}$ host were reported in this work for the first time, so the luminescence properties including critical concentration, critical distance and type of interaction for Dy^{3+} in some hosts [7–16] as well as that in $Sr_3P_4O_{13}:Dy^{3+}$ are listed in Table 1 for comparison, from which it is hard to find some inherent laws of the above three parameters, indicating the different effect of different hosts on the luminescence properties of Dy^{3+} .

The decay curves ($\lambda_{ex} = 349 \text{ nm}$, $\lambda_{em} = 573 \text{ nm}$) of $Sr_{3(1-x)}Dy_{3x}P_4O_{13}$ ($x = 0.005, 0.01, 0.02, 0.03, 0.05$ and 0.1) phosphors were measured and shown in Fig. 4. These decay curves seem not to obey a single-exponential law, which indicates that more than one relaxation process for Dy^{3+} exists in $Sr_3P_4O_{13}:Dy^{3+}$. The process can result from the cross relaxation between Dy^{3+} and Dy^{3+} ions [15, 23]. So all the decay curves were fitted by the double-exponential equation and the average decay time (τ^*) can be calculated in term of the following equations [10, 15] and summarized in Table 2

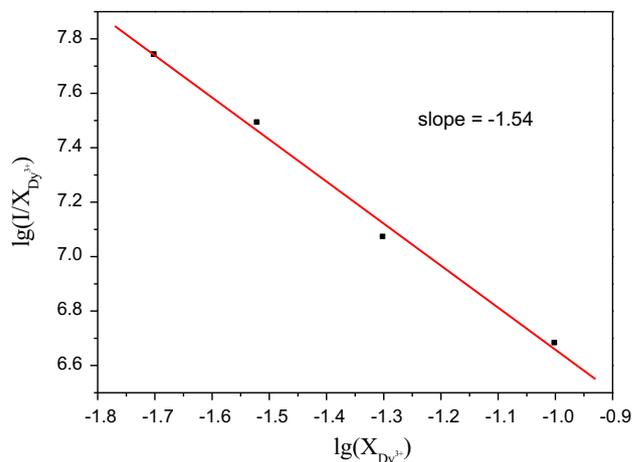
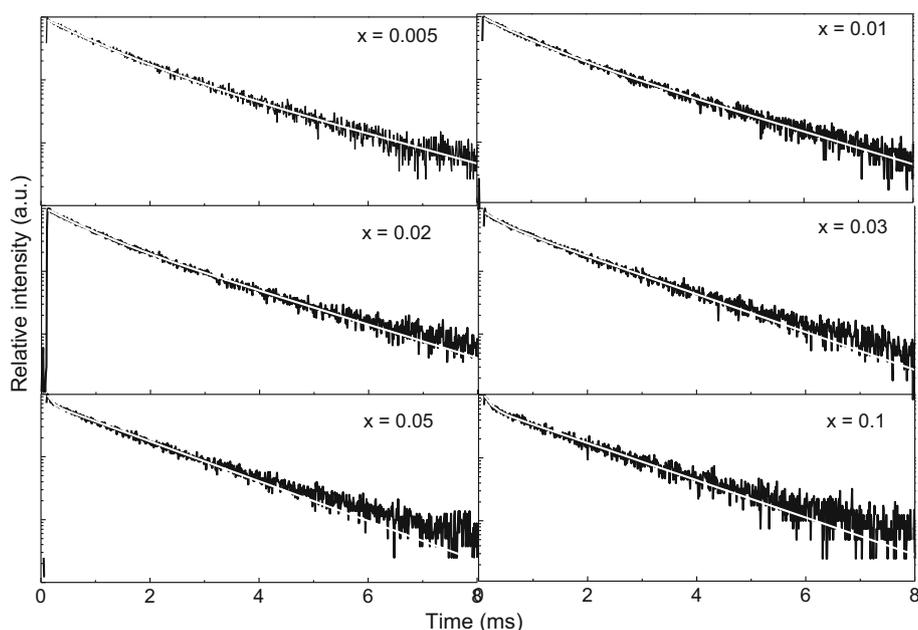


Fig. 3 Curve of $\lg(I/x)$ versus $\lg(x)$ in $Sr_{3(1-x)}Dy_{3x}P_4O_{13}$ phosphors ($\lambda_{ex} = 349 \text{ nm}$)

Table 1 The critical concentration, critical distance and type of interaction for Dy³⁺ in some hosts

Host	Critical concentration	Critical distance (Å)	Type of interaction	Reference
Ca ₃ B ₂ O ₆	0.015	25.32	d–d	7
Ca ₉ Y(VO ₄) ₇	0.3	–	Exchange	8
CaGd ₂ ZnO ₅	0.01	28.81	d–d	9
CaZr ₄ (PO ₄) ₆	0.04	28.9	d–d	10
Mg ₂ SiO ₄	0.03	16.3	d–d	11
MgY ₄ Si ₃ O ₁₃	0.01	20.14	–	12
RbZnPO ₄	0.02	–	Exchange	13
ZnWO ₄	0.015	20.37	–	14
BaNb ₂ O ₆	0.005	39	d–d	15
BiOCl	0.09	8.4	d–d	16
Sr ₃ P ₄ O ₁₃	0.02	29.5	d–d	This work

Fig. 4 Decay curves ($\lambda_{ex} = 349$ nm, $\lambda_{em} = 573$ nm) of Sr_{3(1-x)Dy_{3x}P₄O₁₃ (x = 0.005, 0.01, 0.02, 0.03, 0.05 and 0.1) phosphors}



$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \tag{4}$$

$$\tau^* = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \tag{5}$$

where I is the luminescence intensity; A₁ and A₂ are the constants; t is the time, and τ₁ and τ₂ are the decay times for the exponential components. It can be seen that average decay time is very short (<1.5 ms), and decreases gradually with increasing Dy³⁺ concentration, which could be

interpreted by the increasing excitation energy exchange among Dy³⁺ ions leading to enhance the energy depletion rate [8].

As the sample Sr₃P₄O₁₃:0.02Dy³⁺ shows the much stronger emission intensity and similar emission shape relative to that in other samples, as discussed above, which is chosen as a case to investigate the CIE chromaticity coordinates for the Sr₃P₄O₁₃:Dy³⁺ phosphors. The CIE chromaticity coordinate (x, y) of the sample Sr₃P₄O₁₃:0.02Dy³⁺ is calculated to be (0.345, 0.369) in term of

Table 2 The calculated decay time including τ₁, τ₂ and τ* for the decay curves ($\lambda_{ex} = 349$ nm, $\lambda_{em} = 573$ nm) of Sr_{3(1-x)Dy_{3x}P₄O₁₃ phosphors}

τ	x = 0.005	x = 0.01	x = 0.02	x = 0.03	x = 0.05	x = 0.1
τ ₁ (ms)	0.832	0.725	0.520	0.314	0.123	0.085
τ ₂ (ms)	1.863	1.684	1.634	1.472	1.442	1.371
τ* (ms)	1.384	1.364	1.335	1.304	1.285	1.269

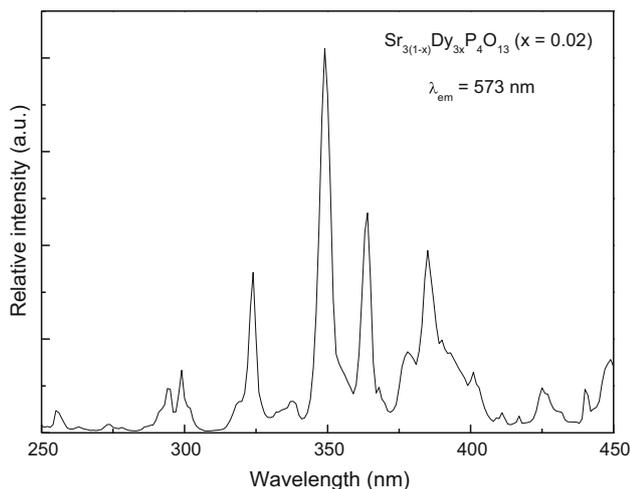


Fig. 5 Excitation spectrum of $\text{Sr}_3\text{P}_4\text{O}_{13}:0.02\text{Dy}^{3+}$ recorded in the spectral range of 250–450 nm

the emission spectrum under 349 nm excitation, which is close to the ideal white standard (0.333, 0.333).

Finally, the excitation spectrum of $\text{Sr}_3\text{P}_4\text{O}_{13}:0.02\text{Dy}^{3+}$ recorded in the spectral range of 250–450 nm is plotted in Fig. 5 by monitoring the emission at 573 nm of Dy^{3+} ion. A series of line-shaped excitation peaks corresponding with the electronic transitions of Dy^{3+} were observed, in which the peak at 349 nm due to the ${}^6\text{H}_{15/2} \rightarrow {}^4\text{M}_{15/2} + {}^6\text{P}_{7/2}$ transition of Dy^{3+} [1] possesses the maximum intensity. The above mentioned characteristics of excitation spectrum indicate the potential application for NUV w-LEDs because of matching partly with the emission of NUV chips [7, 10].

4 Conclusions

In summary, a series of novel single-phase white-light-emitting phosphors $\text{Sr}_3\text{P}_4\text{O}_{13}:\text{Dy}^{3+}$ were synthesized successfully by a solid state reaction at 900 °C for the first time. XRD analysis confirmed pure single-phase formation of $\text{Sr}_3\text{P}_4\text{O}_{13}:\text{Dy}^{3+}$ materials. The optimum concentration of Dy^{3+} ions in $\text{Sr}_3\text{P}_4\text{O}_{13}$ was found around 0.02, and the critical distance of Dy^{3+} was calculated to be about 29.5 Å by investigating the effect of the doping content of Dy^{3+} on the emission intensity of Dy^{3+} . The mechanism of concentration quenching of Dy^{3+} in $\text{Sr}_3\text{P}_4\text{O}_{13}:\text{Dy}^{3+}$ phosphors was confirmed to be dipole–dipole interaction. The average decay time of Dy^{3+} is very short (<1.5 ms), and decreases gradually with increasing Dy^{3+} concentration. The

photoluminescence spectra presented that these phosphors could be excited by NUV light in the region 300–400 nm and emitted white light originating from the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ (485 nm), ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ (573 nm) and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ (663 nm) transitions of Dy^{3+} . The as-obtained results suggested that $\text{Sr}_3\text{P}_4\text{O}_{13}:\text{Dy}^{3+}$ phosphors might be a potential and novel candidate used as single-phase white-light-emitting phosphor for NUV based w-LEDs.

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