



Synthesis and photoluminescence properties of Eu^{2+} doped $\text{Sr}_9\text{Sc}(\text{PO}_4)_7$ phosphors for white light-emitting diodes

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Abstract

A series of Eu^{2+} -activated $\text{Sr}_9\text{Sc}(\text{PO}_4)_7$ yellowish-green emitting phosphors were synthesized by conventional solid-state reaction. The photoluminescence (PL) properties and concentration quenching mechanism of the as-prepared phosphors were investigated. The emission spectrum exhibits a broad and asymmetric band peaking at 510 nm, which corresponds to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} . The excitation spectrum exhibits a broad band extending from 250 to 450 nm, which matches well with the emission of near ultraviolet (n-UV) chips (350–430 nm). Non-radiative transitions between Eu^{2+} ions in the $\text{Sr}_9\text{Sc}(\text{PO}_4)_7$ host have been demonstrated to be attributable to dipole–dipole interactions, and the critical distance was calculated to be 23.1 Å. These results indicate that $\text{Sr}_9\text{Sc}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor could serve as a promising candidate for application in n-UV white-light LEDs.

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1. Introduction

In recent years, phosphate compounds have attracted increasing interest for its promising applications in white-light LEDs. Phosphors based on a phosphate host matrix constitute one of the most important luminescent materials and can impose many crystal-field environments on emission centers. Rare earth ions doped phosphates have excellent thermal stability, and the rigid tetrahedral matrix of the phosphate is thought to be ideal for charge stabilization [1–3]. In addition, the characteristics of easy-synthesis and low-cost are another reasons why these phosphates are considered to be excellent hosts for phosphor materials [4].

The emission and absorption spectra of Eu^{2+} usually consist of broad band due to transitions between the $4f^7$ ground state and $4f^65d^1$ excited state configuration of Eu^{2+} . Since the involved 5d orbital is external, the emission of Eu^{2+} is very strongly dependent on the host lattice. Thus, the host is

very important for the optical properties of Eu^{2+} ions [5,6]. In the past decades, there has been attracting more and more attention on Eu^{2+} -activated phosphates, such as $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Eu}^{2+}$ [7], $\text{Ba}_3\text{Y}(\text{PO}_4)_3:\text{Eu}^{2+}$ [8] and $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7:\text{Eu}^{2+}$ [9]. Herein, we propose that the $\text{Sr}_9\text{Sc}(\text{PO}_4)_7$ host will be an excellent host for phosphor materials. To the best of our knowledge, there is no report on $\text{Sr}_9\text{Sc}(\text{PO}_4)_7:\text{Eu}^{2+}$ as a LED phosphor. In this paper, we report the luminescence properties and mechanism of the concentration quenching of novel yellow-emitting $\text{Sr}_9\text{Sc}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor.

2. Experimental

The $\text{Sr}_{9-x}\text{Sc}(\text{PO}_4)_7$ (SSP): $x\text{Eu}^{2+}$ phosphors were prepared by conventional solid-state reaction. The starting materials were SrCO_3 (99.9%), Sc_2O_3 (99.99%), $(\text{NH}_4)_2\text{HPO}_4$ (99%) and Eu_2O_3 (99.99%). The stoichiometric amounts of starting materials were thoroughly ground in an agate mortar, and the homogeneous mixture was transferred to an alumina crucible and calcined in a furnace at 1400 °C for 4 h under a reducing atmosphere of 5% $\text{H}_2/95\%$ N_2 .

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Powder X-ray diffraction (XRD) data was collected using Cu-K α radiation (1.54056 Å) on a Bruker D8 advance diffractometer. The photoluminescence (PL), photoluminescence excitation (PLE) and diffuse reflectance (DR) spectra were characterized by a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150 W Xe lamp as the excitation source.

3. Results and discussion

Fig. 1 shows the XRD patterns of SSP: $x\text{Eu}^{2+}$ ($x=0.005, 0.01, 0.03, 0.05, 0.07, 0.10, 0.15, 0.20$) samples. All the diffraction peaks can be indexed to the JCPDS data of $\text{Sr}_9\text{Sc}(\text{PO}_4)_7$ (No. 54-1186). This result indicates that doping Eu^{2+} into SSP host does not generate any impurity phase.

Fig. 2 shows the excitation and emission spectra of SSP:0.10 Eu^{2+} phosphor. The excitation spectrum ranging from 250 to 450 nm is composed of three broad absorption bands around 300, 330, and 390 nm, attributed to $4f^7 \rightarrow 4f^65d^1$ transitions of the Eu^{2+} ions [10]. Under 365 nm excitation, the emission spectrum exhibits broad band extending from 410 to 750 nm and peaking at 510 nm, which is due to the electric-dipole allowed $4f-5d$ transition of the Eu^{2+} ions.

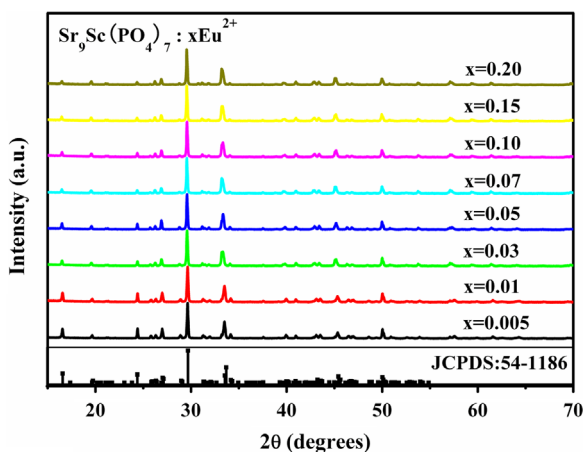


Fig. 1. The XRD patterns of SSP: $x\text{Eu}^{2+}$ ($0.005 \leq x \leq 0.20$).

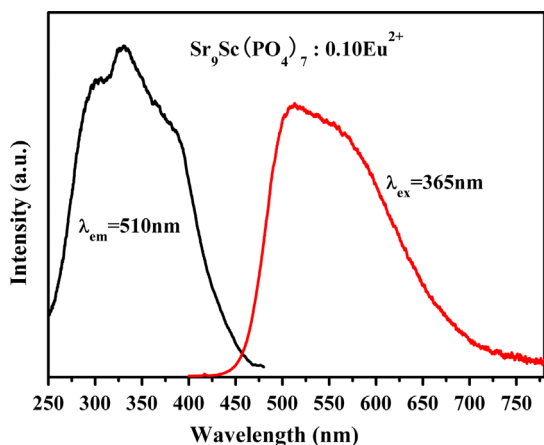


Fig. 2. PLE ($\lambda_{em}=510$ nm) and PL ($\lambda_{ex}=365$ nm) spectra for SSP:0.10 Eu^{2+} .

The reflectance spectra of SSP: $x\text{Eu}^{2+}$ ($0 \leq x \leq 0.20$) are shown in Fig. 3. The SSP shows energy absorption in the ≤ 350 nm region, and the band gap was estimated to be about 3.94 eV (315 nm). As doping Eu^{2+} ions into the SSP, a strong broad absorption in the 200–450 nm near-UV range can be observed, which is assigned to the $4f^7 \rightarrow 4f^65d^1$ absorption of the Eu^{2+} ions. The absorption edge gradually extends to longer wavelengths, and the absorption is enhanced for higher Eu^{2+} ion concentrations, resulting in an overall red shift of the excitation wavelength to 450 nm. The absorption band matches well with near-UV chips for applications in white-light near-UV LEDs.

In order to obtain the optimum doping concentration of Eu^{2+} ions, a series of SSP: $x\text{Eu}^{2+}$ ($0.005 \leq x \leq 0.20$) phosphors were prepared. Fig. 4 shows the emission spectra of the samples. Under 365 nm excitation, the emission intensity first increases with the growth of Eu^{2+} concentration and then decreases. When $x=0.10$, the emission intensity reaches the maximum.

The emission intensity decreases with increasing Eu^{2+} concentration for $x \geq 0.10$, which is induced by the energy transfer between Eu^{2+} ions in the phosphors. The critical distance of energy transfer (R_c) can be estimated by Blasse using the following

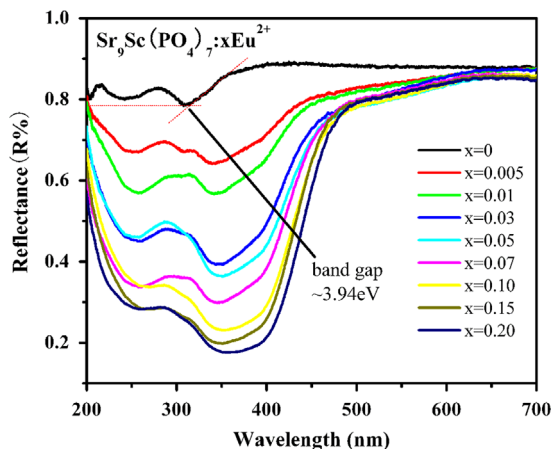


Fig. 3. Reflectance spectra of SSP: $x\text{Eu}^{2+}$ ($0.005 \leq x \leq 0.20$) phosphors.

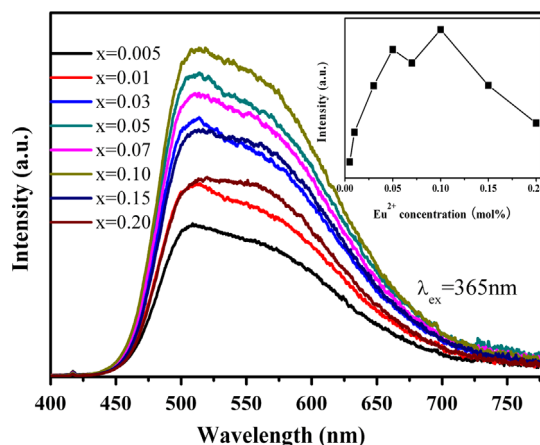


Fig. 4. PL emission spectrum of SSP: $x\text{Eu}^{2+}$ phosphors under 365 nm excitation. The inset shows the dependence of emission intensity of SSP: $x\text{Eu}^{2+}$ on the Eu^{2+} concentration.

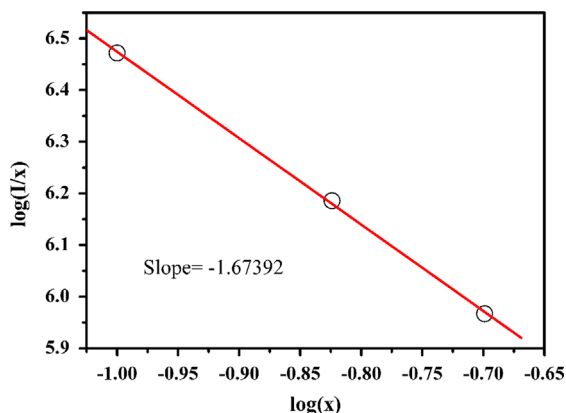


Fig. 5. The curve of $\log I/x$ vs. $\log x$ in $\text{SSP}:x\text{Eu}^{2+}$ phosphor.

equation [11]

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

where x_c is the critical concentration, N is the number of cations in the unit cell and V is the volume of the unit cell. According to the experimental and analytic values of V , N and x_c (2580.855 \AA^3 , 4, 0.10, respectively), the critical transfer distance of Eu^{2+} in SSP phosphor is calculated to be about 23.1 \AA .

Concentration quenching usually occurs as a result of non-radiative energy transfer among luminescent centers. According to the report of Van Uitert, the energy transfer usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole–multipole interaction [12]. The R_c of $\text{SSP}:\text{Eu}^{2+}$ phosphor is longer than 5 \AA , it indicates that the mechanism of exchange interaction plays no role in energy transfer between Eu^{2+} ions in the $\text{SSP}:x\text{Eu}^{2+}$ phosphor. Considering that the radiation reabsorption is only due to the spectral overlap, however, as shown in Fig. 2, there is not obviously spectral overlap between the emission and excitation bands of Eu^{2+} ions. Therefore, the concentration quenching process in $\text{SSP}:\text{Eu}^{2+}$ phosphor is probably due to multipole–multipole interaction. The mechanism of interaction between the Eu^{2+} ions can be expressed by the following equation [12]

$$I/x = K \left[1 + \beta(x)^{\theta/3} \right]^{-1} \quad (2)$$

where x is the activator concentration; K and β are constants for each interaction for a given host lattice. According to the research result of Van Uitert, $\theta=3$ for the energy transfer among the nearest-neighbor ions, as $\theta=6$, 8, and 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. To get a correct θ value for the emission center, the dependence of $\lg(I/x)$ on $\lg(x)$ is plotted, and it yields a straight line with a slope equal to $-\theta/3$. From Fig. 5, the slope was determined to be -1.67392 . The value of θ can be calculated as 5.02, which is approximately equal to 6. The result indicates that non-radiative transitions between Eu^{2+} ions occur via dipole–dipole interactions and lead to

concentration quenching of the Eu^{2+} ions in the $\text{SSP}:x\text{Eu}^{2+}$ phosphors.

4. Conclusion

In summary, novel yellowish-green-emitting phosphors $\text{Sr}_9\text{Sc}(\text{PO}_4)_7:x\text{Eu}^{2+}$ were synthesized, and their luminescence properties, diffuse reflectance spectra were investigated. The as-prepared phosphors exhibit a strong absorption broad in the 200–450 nm range, which matches well with those of NUV LED chips, and an intense yellowish-green emission band with a main peak at 510 nm. Non-radiative transitions between the Eu^{2+} ions in the $\text{Sr}_9\text{Sc}(\text{PO}_4)_7$ host are attributable to dipole–dipole interactions, and the critical distance was determined to be 23.1 \AA . The above results indicate that $\text{Sr}_9\text{Sc}(\text{PO}_4)_7:x\text{Eu}^{2+}$ phosphors are promising to develop possible applications for white LEDs.

Acknowledgments

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