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Color-tunable luminescence and energy transfer of Eu^{2+}/Mn^{2+} co-doped $Sr_9Lu(PO_4)_7$ phosphors for white LEDs

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ABSTRACT

A series of Eu^{2+} and Mn^{2+} activated novel $Sr_9Lu(PO_4)_7$ phosphors has been prepared through a high temperature solid state reaction. The obtained samples show a strong excitation band between 250 and 450 nm, which is in good agreement with near-ultraviolet (NUV) LED chips. Upon excitation at 365 nm, the $Sr_9Lu(PO_4)_7$:Eu^{2+} phosphor exhibits a broad yellowish-green emission band which peaks at 530 nm. In the Eu^{2+} and Mn^{2+} ions co-doped phosphors $Sr_9Lu(PO_4)_7$:Eu^{2+}, Mn^{2+}, tunable colors from yellowish-green to yellow can be obtained by varying the content of the Mn^{2+} ion. Additionally, energy transfer from the Eu^{2+} to Mn^{2+} ions is proven to follow a dipole–quadrupole mechanism according to the decay curves. These results indicate that the $Sr_9Lu(PO_4)_7$:Eu^{2+}, Mn^{2+} phosphors could applicable for NUV based white light-emitting diodes.

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1. Introduction

White light-emitting diodes (W-LEDs) have received increasing attention not only in scientific areas but also in the technical industry due to their outstanding advantages, such high brightness, low power consumption, great stability, long operating and good environmentally friendly traits [1–4]. At present, the mainstream commercial W-LEDs in the market are fabricated by combining InGaN LED chips and yellow emitting $Y_3Al_5O_{12}$:Ce^{3+} phosphors. Nevertheless, this kind of white light suffers from a low color rendering index and a high correlated color temperature due to the lack of a red spectral component in the visible region [5,6]. At present, W-LEDs fabricated using NUV chips (380–420 nm) coupled with a blend of yellow- and blue-emitting phosphors have revealed outstanding properties, such as tunable correlated color temperature, tunable Commission International de l'Eclairage (CIE) chromaticity coordinates and an excellent color rendering index [7]. As a result, it is still necessary to develop novel phosphors that can be effectively excited in the NUV range.

Recently, phosphate has attracted more and more attention as a luminescent host material due to its great thermal and charge stabilization. At present, a variety of compounds that are structurally similar to $Sr_9A(PO_4)_7$ have been reported in the literature, such as $Sr_9Sc(PO_4)_7$ [8], $Sr_8MgSc(PO_4)_7$ [9], $Sr_8MgGd(PO_4)_7$ [10] and $Sr_8ZnSc(PO_4)_7$ [11]. Herein, we propose that the $Sr_9Lu(PO_4)_7$ host will be an excellent host for phosphor materials. To the best of our knowledge, there is no report on $Sr_9Lu(PO_4)_7$:Eu^{2+}, Mn^{2+} as a LED phosphor. Therefore, we prepared $Sr_9Lu(PO_4)_7$:Eu^{2+}, Mn^{2+} phosphor by a conventional high temperature solid state reaction. The luminescence properties and energy transfer mechanism from the Eu^{2+} to Mn^{2+} ions in $Sr_9Lu(PO_4)_7$ host have been studied.

2. Experimental approach

2.1. Sample preparation

The $Sr_{9-x-y}Lu(PO_4)_7$:xEu^{2+}, yMn^{2+} (x, y represent the concentration of Eu^{2+} and Mn^{2+} ions, respectively) phosphors were prepared by a high temperature solid state reaction. The starting materials were $SrCO_3$ (99%), Lu_2O_3 (99%), $NH_4H_2PO_4$ (99%), Eu_2O_3 (99.99%) and MnO_2 (85%), 5 wt% of H_3BO_3 (99%) was added as a flux. The starting reagents were thoroughly mixed in stoichiometric proportions and ground for 1 h in an agate mortar. The mixture was preheated in air at 600 °C for 3 h, reground and then sintered at 1290 °C for 3 h in a reducing CO atmosphere.

2.2. Characterization

The X-ray diffraction (XRD) pattern was collected on an X-ray diffractometer (Japan, Shimadzu, XRD-6000) with Cu Kα radiation (λ = 0.15406 nm) over the angular range $10° \le 2\theta \le 60°$, operating at 40 kV and 30 mA. Diffuse reflection spectra were obtained by a

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UV–Vis spectrophotometer (Shimadzu, UV-2600) using the white powder $BaSO_4$ as a reference. The photoluminescence excitation/emission spectra were measured using an Edinburgh FLS-980 fluorescence spectrophotometer equipped with a 450 W xenon lamp as an excitation light source. The luminescence decay curves of the samples were measured using a Fluorescence lifetime measurement system (Horiba DeltaPro) with a NanoLED source (λ = 370 nm).

3. Results and discussion

Fig. 1 shows the typically XRD patterns of the $Sr_9Lu(PO_4)_7$ host and the $Sr_9Lu(PO_4)_7$:0.05Eu^{2+}, $Sr_9Lu(PO_4)_7$:0.20Eu^{2+} and $Sr_9Lu(PO_4)_7$:0.05Eu^{2+}, 0.15Mn^{2+} samples, as well as the standard patterns of $Sr_9In(PO_4)_7$ (COD-ID 53-179). It is obviously that no extra phase was observed. The results indicate that the $Sr_9Lu(PO_4)_7$ host was a single phase and that doping with a small amounts of Eu^{2+} and Mn^{2+} ions did not induce any significant changes of the crystal structure.

The reflectance spectra of the $Sr_9Lu(PO_4)_7$, $Sr_9Lu(PO_4)_7$:0.1Eu^{2+} and $Sr_9Lu(PO_4)_7$:0.1Eu^{2+}, 0.1Mn^{2+} phosphors are shown in Fig. 2. Apparently, the $Sr_9Lu(PO_4)_7$ host material exhibits an absorption band from 200 to 400 nm, which is the host absorption. When Eu^{2+} ions are doped in the $Sr_9Lu(PO_4)_7$ host, two obvious absorption bands from 230 to 450 nm can be observed. Moreover, with the introduction of Mn^{2+} ions in the former $Sr_9Lu(PO_4)_7$:0.1Eu^{2+} phosphor, the shape of the reflectance spectrum remained unchanged, only the intensity increased a little. Fig. 2 indicates the $Sr_9Lu(PO_4)_7$:Eu^{2+}, Mn^{2+} phosphor has a strong absorption band from the ultraviolet to blue region, which is in good agreement with commercial NUV LEDs (360–410 nm) [12].

The band gap of the $Sr_9Lu(PO_4)_7$ host can be calculated from Eq. (1) [13]:

$$F(R_\infty h\nu)^n = A(h\nu - E_g) \quad (1)$$

where $h\nu$ is the photon energy, A is a constant that depends on the properties of the material, $[F(R_\infty)h\nu]^2 = 0$ is the Kubelka–Munk function which is defined as [14]:

$$F(R_\infty) = (1-R)^2/2R = K/S \quad (2)$$

where K, R and S are the absorption, reflection and scattering coefficients, respectively. The linear extrapolation in the inset of Fig. 2 shows a band gap value of about 3.91 eV.

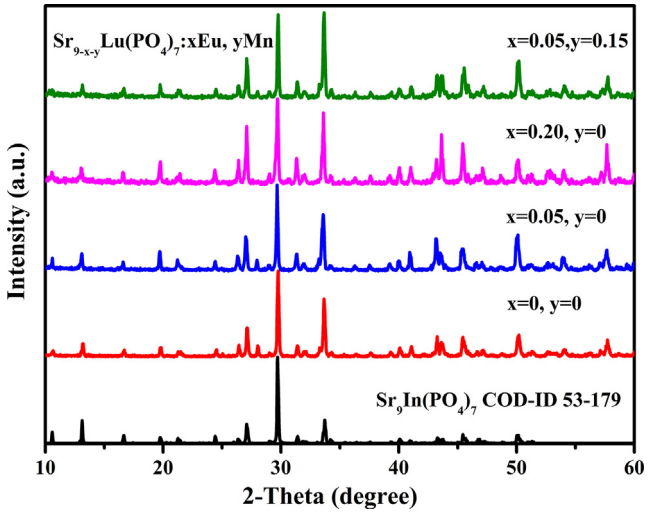

Fig. 1. XRD profiles of the $Sr_9Lu(PO_4)_7$ host and the $Sr_9Lu(PO_4)_7$:0.05Eu^{2+}, $Sr_9Lu(PO_4)_7$:0.20Eu^{2+} and $Sr_9Lu(PO_4)_7$:0.05Eu^{2+}, 0.15Mn^{2+} phosphors.

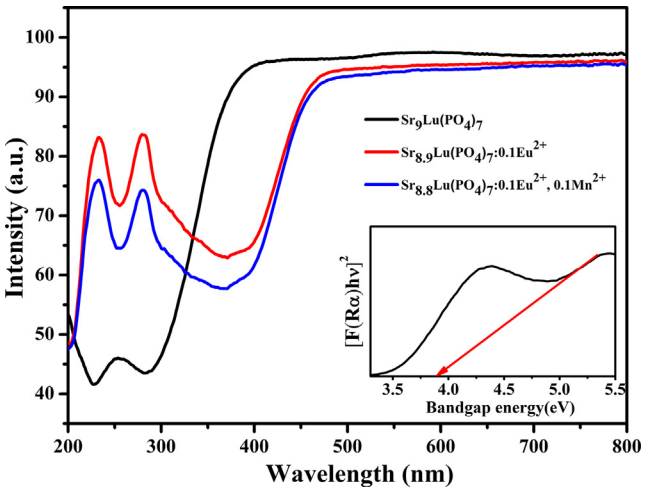

Fig. 2. Diffuse reflectance spectra of the $Sr_9Lu(PO_4)_7$ host and the $Sr_9Lu(PO_4)_7$:0.1-Eu^{2+} and $Sr_9Lu(PO_4)_7$:0.1Eu^{2+}, 0.1Mn^{2+} phosphors; the inset shows the extrapolation of the band gap energy for the host.

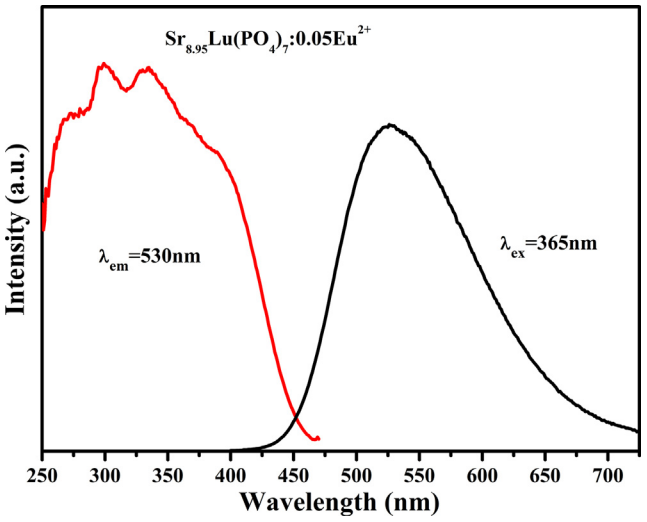

Fig. 3. Excitation (λ_{em} = 530 nm) and emission (λ_{ex} = 365 nm) spectra for $Sr_9Lu(PO_4)_7$:0.10Eu^{2+}.

Fig. 3 shows the excitation and emission spectra of the $Sr_9Lu(PO_4)_7$:0.05Eu^{2+} phosphor. On monitoring the emission at 530 nm, the excitation spectrum shows broad absorption bands ranging from 250 to 450 nm due to the $4f^7 \rightarrow 4f^65d^1$ transitions of the Eu^{2+} ions. The excitation spectrum indicates that the phosphor matches well with the commercial NUV LED chips (360–410 nm) [15]. Under excitation at 365 nm, the $Sr_9Lu(PO_4)_7$:0.05Eu^{2+} phosphor shows a bright yellowish-green emission and the emission spectrum exhibits a wide emission band covering 410–725 nm, with the maximum at around 530 nm, which is assigned to the $4f^65d \rightarrow 4f^7$ transition of the Eu^{2+} ions.

To study the influence of the doping concentration of the Eu^{2+} ions on the emission intensity of the phosphors, a series of $Sr_9Lu(PO_4)_7$:xEu^{2+} ($0.005 \leq x \leq 0.20$) phosphors have been synthesized. Fig. 4 shows the emission spectra of the samples under radiation of 365 nm. By comparing the emission spectra, there are no obvious differences for the spectral profiles and positions except for the intensity. It is obvious that the optimal Eu^{2+} ion concentration is when x = 0.05, and the emission intensity of the samples starts to decay beyond this Eu^{2+} ion concentration due to concentration quenching [16].

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