



Energy transfer and color tunable emission in Tb³⁺, Eu³⁺ co-doped Sr₃LaNa(PO₄)₃F phosphors



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ABSTRACT

A group of color tunable Sr₃LaNa(PO₄)₃F:Tb³⁺,Eu³⁺ phosphors were prepared by conventional high temperature solid state method. The phase structures, luminescence properties, fluorescence lifetimes and energy transfer were investigated in detail. Under 369 nm excitation, owing to efficient energy transfer of Tb³⁺ → Eu³⁺, the emission spectra both have green emission of Tb³⁺ and red emission of Eu³⁺. An efficient energy transfer occur in Tb³⁺, Eu³⁺ co-doped Sr₃LaNa(PO₄)₃F phosphors. The most possible mechanism of energy transfer is dipole-dipole interaction by Dexter's theoretical model. The energy transfer of Tb³⁺ and Eu³⁺ was confirmed by the variations of emission and excitation spectra and Tb³⁺/Eu³⁺ decay lifetimes in Sr₃LaNa(PO₄)₃F:Tb³⁺,Eu³⁺. The color tone can tuned from yellowish-green through yellow and eventually to reddish-orange with fixed Tb³⁺ content by changing Eu³⁺ concentrations. The results show that the prepared Tb³⁺, Eu³⁺ co-doped color tunable Sr₃LaNa(PO₄)₃F phosphor can be used for white LED.

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1. Introduction

The white light emitting diodes (LEDs) with advantages of high brightness, small volume, long service life, high efficiency, energy saving, and green environmental protection arouses people's wide attention [1–3]. However, the commercialized method to realize white light is to combine a yellow emitting phosphor Y₃Al₅O₁₂:Ce³⁺ (YAG: Ce³⁺) with blue emitting InGaN chips. Noteworthy, due to the intrinsic lack of red component this devices has presented some inherent drawbacks such as low luminous efficiency, poor color rendering index (CRI), high correlated color temperature (CCT) and so on [4–6]. Currently, the predominant way to yield white light with excellent color rendering indexes is combining a UV chip with red, green, and blue phosphors [7,8]. Either color tunable phosphors or a single-phase phosphor can generate red, green, and blue emissions [9,10]. So, it is imperative to develop novel intense emission tricolor phosphors under near-UV excitation.

Tb³⁺ or Eu³⁺ doped phosphors arise wide practical applications in lightings and displays. Eu³⁺ is an important activator of rare earth activated red emitters, due to Eu³⁺ ions activated red phosphors have appropriate CIE chromaticity coordinates and great luminescent properties. However, they also have some drawback such as exist only weak absorption in near-UV and blue regions [11,12]. The electrons of Eu³⁺ ions shift from the ⁷F₃ ground state to the ⁵D₃, ⁵L₃ and ⁵G₃ excited states are all parity-forbidden [13,14]. Therefore, it is imperative to

find an appropriate sensitizer to enhance the luminescence intensity of Eu³⁺ [15,16]. Energy transfer (ET) from a sensitizer to an activator has been aroused wide attention for the reason that it can obtain color tunable or white emitting phosphors [17–19]. Tb³⁺ is one of the most suitable sensitizer for Eu³⁺ because the absorption wavelength of Eu³⁺ matches the emission wavelength of Tb³⁺, so the energy transfer from Tb³⁺ to Eu³⁺ is efficient. In recent years, energy transfer among Tb³⁺ and Eu³⁺ in a proper host have attracted significant interest because of its good luminescence properties and color reproducibility [20]. In previous reports Tb³⁺ and Eu³⁺ co-doped phosphors could generated white light or multicolor tunable light used for light emitting diodes (LEDs), PDPs and FEDs. In addition, Tb³⁺, Eu³⁺ co-doped phosphors can emit green, yellow, red light by simply adjusting the ratio of Tb³⁺ and Eu³⁺, for example CaYAlO₄:Tb³⁺/Eu³⁺ [21], KCaY(PO₄)₂:Tb³⁺,Eu³⁺ [22], Li BaB₉O₁₅ [23] and La₃GaGe₅O₁₆:Tb³⁺,Eu³⁺ [24]. Turning the color output according to the requirements of practical application become more and more convenient.

In recent years, fluorophosphates become the most important phosphors host because they have many excellent properties such as intensity luminescence, low synthesis temperature and high chemical stability [25,26]. Recently, Hu et al. prepared Sr₃NaLa(PO₄)₃F:Eu²⁺, Mn²⁺ [27] phosphors and reported their luminescence properties. In our study, we investigate the phase structures, luminescence properties, fluorescence lifetimes, energy transfer of Sr₃LaNa(PO₄)₃F:0.20Tb³⁺,nEu³⁺ phosphor. The energy transfer of Tb³⁺ and Eu³⁺ was confirmed by the variations of emission and excitation spectra and Tb³⁺/Eu³⁺ decay lifetimes in Sr₃LaNa(PO₄)₃F:Tb³⁺,Eu³⁺. Furthermore, the energy

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transfer allows the tunable emissions, so can change the concentrations ratio of Tb^{3+}/Eu^{3+} to generate color tunable phosphors.

2. Experimental

2.1. Materials and Synthesis

A group of $Sr_3La_{(1-0.20-n)}Na(PO_4)_3F:0.20Tb^{3+},nEu^{3+}$, (SLN:0.20 Tb^{3+},nEu^{3+} , $n = 0-0.20$) phosphors were synthesized by high temperature solid state reaction. The raw materials $SrCO_3$ (A.R.), SrF_2 (A.R.), La_2O_3 (A.R.), $NaHCO_3$ (A.R.), $NH_4H_2PO_4$ (A.R.), Eu_2O_3 (99.99%), and Tb_4O_7 (99.99%) were weighed according to the particular stoichiometric ratio with 20% excess of SrF_2 due to the loss of fluorine. Mixing and grinding the starting materials in an agate mortar for 30 min and then put the mixture in a crucible sintered at 1000 °C for 2 h in air atmosphere. Finally, the synthesized samples were slowly cooled to room temperature and reground for further measurements.

2.2. Measurements and Characterization

The powder X-ray diffraction (XRD) measurements were performed on D8 Focus diffractometer (Bruker) with graphite monochromatized Cu K α radiation ($\lambda = 0.15405$ nm) operating at 40 kV and 40 mA. A step size of 2θ was 0.02° used with a scanning speed of $10^\circ \text{ min}^{-1}$ with 2θ range from 10° to 80° . The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the obtained powders were recorded with a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The luminescence decay curve was obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1GHz) using a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO). All of the measurements mentioned above were performed at room temperature.

3. Results and Discussion

3.1. Phase Identification

Fig. 1 depicts the X-ray powder diffraction (XRD) patterns of the series of SLN:0.20 Tb^{3+},nEu^{3+} ($n = 0-0.20$) phosphors. $Sr_3LaNa(PO_4)_3F$ has a belovite-type crystal structure with space group $p3$ (No.147), lattice parameters of $a = 9.666$ Å, $b = 9.666$ Å, $c = 7.177$ Å, $V = 580.72$

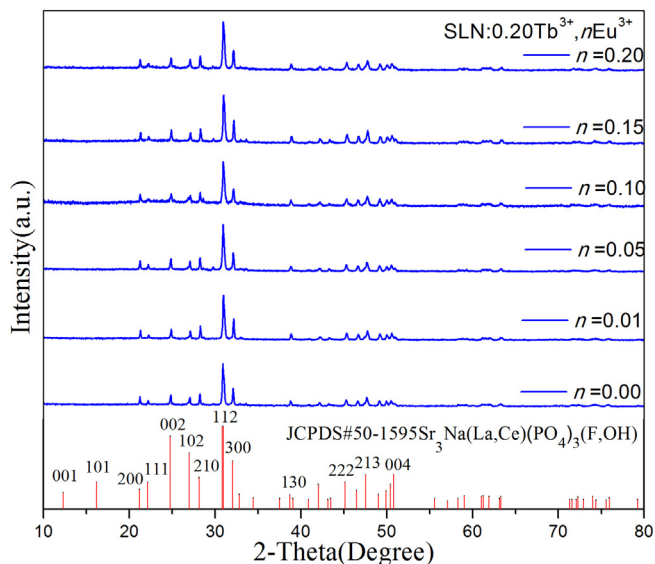


Fig. 1. Powder XRD patterns for SLN:0.20 Tb^{3+},nEu^{3+} ($n = 0-0.20$) phosphors. The standard data for $Sr_3Na(La,Ce)(PO_4)_3(F,OH)$ (JCPDS card no.50-1595) as shown as a reference.

Å³ and $Z = 2$. The results show that all peaks can be indexed to the phases of $Sr_3Na(La,Ce)(PO_4)_3(F,OH)$ (JCPDS card No.50-1595), indicating that the developed samples are single phase and co-doped Tb^{3+} and Eu^{3+} ions do not lead to any significant change in the host structure. There are almost no shift of the XRD peaks of the $Sr_3LaNa(PO_4)_3F$ phosphors in compare with the standard data of $Sr_3Na(La,Ce)(PO_4)_3(F,OH)$ were presented in Fig. 1. According to the reference $Sr_3GdNa(PO_4)_3F:Eu^{2+},Mn^{2+}$ [27], in the $Sr_3LaNa(PO_4)_3F: Tb^{3+}, Eu^{3+}$ system, it is assumed that both the Eu^{3+} ($r = 1.12$ Å when CN = 9) ions and Tb^{3+} ($r = 1.095$ Å when CN = 9) ions occupied the La^{3+} ($r = 1.22$ Å when CN = 9) position, due to the similarity of valence and ionic radius.

3.2. Photoluminescence Properties

Fig. 2 shows the excitation and emission spectra of SLN:0.20 Tb^{3+} . The excitation spectrum, monitoring at 545 nm, contains a list of spectral bands from 200 nm to 400 nm. 4f-5d transitions of Tb^{3+} ion lead to broad bands at ~230 nm. The sharp peaks could be appropriately according to the 4f-4f forbidden transitions of Tb^{3+} , i.e. $^7F_6-^5H_6$ at 305 nm, $^7F_6-^5H_7$ at 318 nm, $^7F_6-^5D_2$ at 341 and 352 nm, and $^7F_6-^5G_6$ at 369 and 378 nm [28]. In these excitation peaks, the strongest peak at 369 nm is chosen to excitation wavelength for strong emission. In emission spectrum, the peaks appearing in 492 nm, 545 nm, 586 nm, and 623 nm are correspond to $^5D_4-^7F_J$ ($J = 6, 5, 4, 3$) transitions, respectively. It has the strongest intensity at 545 nm which is in green emission range largest probability attributed to electric-dipole transition.

The excitation and emission spectra of SLN:0.05 Eu^{3+} was shown in Fig. 3. The excitation spectrum reveals a broadband from 200 to 310 nm (with a strongest excitation peak at about 265 nm) and several sharp peaks located at 319 nm ($^7F_0-^5H_5$), 361 nm ($^7D_0-^5D_4$), 382 nm ($^5D_0-^5L_6$), 393 nm ($^7F_0-^5L_6$), 415 nm ($^7F_0-^5D_3$), 464 nm ($^7F_0-^5D_2$), respectively. The broadband from 200 to 310 nm can be attributed to charge transfer band (CTB) from negative oxygen ion ($2p^6$) to the empty state of $4f$ of Eu^{3+} ion. The emission spectrum of SLN: Eu^{3+} contains several typical emission peaks be assigned to the transition from 5D_0 excited state to the ground state of 7F_J ($J = 1, 2, 3, 4$) of Eu^{3+} [29]. The orange emission peak at 592 nm is ascribed to $^5D_0-^7F_1$ transition, while the dominant red emission peak at 618 nm is due to the $^5D_0-^7F_2$ transition, upon excitation with 394 nm light. Both the $^5D_0-^7F_2$ transition and the $^5D_0-^7F_4$ transition corresponding to forced electric dipole, so sample SLN:0.05 Eu^{3+} show almost equal intensity in 592 nm and 702 nm. The high intensity of the $^5D_0-^7F_4$ transition has been also

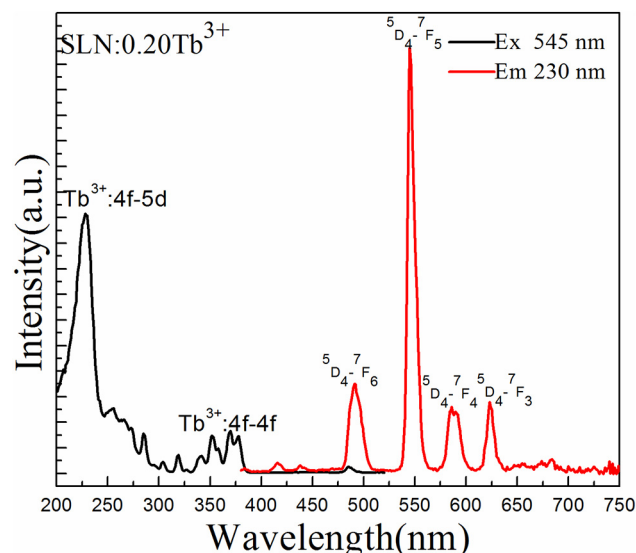


Fig. 2. Excitation and emission spectra of SLN:0.20 Tb^{3+} phosphor.

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