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Study on luminescence and thermal stability of blue-emitting $Sr_5(PO_4)_3F$: Eu^{2+}phosphor for application in InGaN-based LEDs

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ABSTRACT

A series of blue-emitting phosphors $Sr_5(PO_4)_3F$: Eu^{2+} were synthesized by traditional high temperature solid-state reaction method. The micro-morphology and photoluminescence properties of the phosphors were investigated. The $Sr_5(PO_4)_3F$: Eu^{2+} phosphors exhibit broad excitation spectra ranging from 250 to 420 nm, and an intense asymmetric blue emission band peaking at 435 nm. Two different Eu^{2+} emission centers in $Sr_5(PO_4)_3F$: Eu^{2+} phosphors were confirmed *via* their fluorescence properties. The concentration quenching mechanism, fluorescence lifetime and thermal stability of $Sr_5(PO_4)_3F$: Eu^{2+} phosphors were studied in detail. The thermal stability can be improved obviously by anion substitution. The CIE chromaticity coordinates of $Sr_5(PO_4)_3F$: Eu^{2+} phosphors with different Eu^{2+}-doped concentrations were calculated. A blue light-emitting diode was fabricated by combination of a 370 nm InGaN chip and the prepared phosphor $Sr_5(PO_4)_3F$: Eu^{2+}. The present work suggests that $Sr_5(PO_4)_3F$: Eu^{2+} is a potential phosphor applied in InGaN-based LEDs.

1. Introduction

White light-emitting diodes (WLEDs) are considered as the new generation solid-state lighting sources due to their many advantages such as high energy efficiency, long lifetime, light stability and environmental friendliness [1–3]. At present, commercial WLEDs are combination of blue InGaN chip and yellow phosphor (YAG: Ce^{3+}) [4,5]. However, this method suffers a low color rendering index ($R_a < 80$) and high correlated color temperature ($T_c > 4500$ K) because the deficiency of red component in the visible region [6–9]. In order to improve the color rendering index (CRI), blue, green and red multi-phased phosphors pumped by ultraviolet/near-ultraviolet (UV/NUV) chips have been proposed and studied intensively [10–12]. The eventual performance of this type of WLEDs is based on the properties of phosphors strongly. Therefore, it is highly desirable to develop new phosphors that can be effectively excited by UV/NUV chips [13–16].

The luminescence properties of Eu^{2+} have been widely investigated in various hosts [17]. As is known to all, Eu^{2+} shows broad excitation and absorption spectra due to the $4f^7$of ground state and $4f^65d^1$of excited state, respectively. Because the $5d$ energy levels of the Eu^{2+} ions are sensitive to the crystal field, it is very likely to design a phosphor with special emission color by finding a suitable compound to provide sites to be occupied by Eu^{2+} [18–20]. The luminescence characteristics are significantly dependent on the type of host crystal [21]. Rare earth ions doped phosphate compounds as the luminescence materials have been widely investigated, owing to their good physical and chemical stability, cheap raw materials and mild preparation conditions [22]. Therefore, Eu^{2+}-activated phosphate phosphors have attracted growing interest due to the above-mentioned advantages of phosphate host and activator Eu^{2+} [23].

$Sr_5(PO_4)_3F$ belongs to the apatite-type structure and there are two kinds of Sr^{2+} ions sites (Sr1 and Sr2) with different coordination environments in $Sr_5(PO_4)_3F$ lattice. Sr1 is the Wyckoff symbol $4f$ site coordinated by 9 oxygen atoms, and Sr2 is the $6h$ site coordinated by 7 oxygen atoms and one fluorine atom [24]. In 2009, Dhoble et al. reported the photoluminescence properties of Eu^{2+} ion in $M_5(PO_4)_3F$ (M = Ba, Sr, Ca) [25]. Then, they studied the energy transfer between Ce^{3+} and Eu^{2+} in doped $Sr_5(PO_4)_3F$ phosphor [26]. In 2012, Swart et al. reported the identification of Eu oxidation states in a doped $Sr_5(PO_4)_3F$ phosphor by TOF-SIMS imaging [27]. In 2015, Huang et al. studied the energy transfer from the Eu^{2+} to Mn^{2+} in $Sr_5(PO_4)_3F$: Eu^{2+}, Mn^{2+} phosphors and the enhancement of white-light-emission by flux [28].

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However, few studies have been done on thermal stability and application of $Sr_5(PO_4)_3F$: Eu^{2+} phosphor in InGaN-based LEDs. In this study, a series of blue phosphate phosphors $Sr_{5(1-x)}(PO_4)_3F$: $5xEu^{2+}$ ($x = 0.004$, 0.008,0.010, 0.012, 0.016) and $Sr_5(PO_4)_3Cl$: Eu^{2+} were prepared by solid-state method. Also, micro-morphology, photoluminescence properties, thermal stability and application in InGaN-based LEDs were investigated in detail. The phosphors show intense blue emission peaking at 435 nm under UV/NUV light (250–420 nm) excitation. Moreover, the $Sr_5(PO_4)_3F$: Eu^{2+} phosphors exhibit high color purity and good color stability.

2. Experimental section

2.1. Materials and Synthesis

The designed $Sr_{5(1-x)}(PO_4)_3F$: $5xEu^{2+}$ ($x = 0.004$, 0.008,0.010, 0.012, 0.016) phosphors and $Sr_{4.95}(PO_4)_3Cl$: $0.050Eu^{2+}$ phosphor used for comparison were synthesized by conventional high temperature solid-state reaction. The starting materials were as follows: $SrCO_3$ (A.R.), SrF_2 (A.R.), $SrCl_2$ (A.R.), $NH_4H_2PO_4$ (A.R.) and Eu_2O_3 (99.99% purity). First, the starting materials were mixed and ground according to stoichiometric ratio in an agate mortar for 15–20 min. Then, the mixture was transferred to a crucible and sintered at 800 °C for 3 h in a CO reductive atmosphere. After that, we obtained the final phosphors for further measurements.

2.2. Characterization

Crystal phase identification was carried out on X-ray diffractometer (XRD, D-MAX2500/PC, RIGAKU Corporation, Japan) using 40 kV, 20 mA and Cu K_α radiation ($\lambda = 1.5406$ Å). Microtopography of the calcined particles was observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan). Excitation and emission spectra, temperature-dependent luminescence, the quantum efficiency and fluorescence lifetime were measured by time-resolved and steady-state fluorescence spectrometers (FLS920, Edinburgh Instruments, UK) equipped with a 450 W Xe lamp, a 150 W nF900 flash lamp.

2.3. LED measurements

To fabricate LED, $Sr_5(PO_4)_3F$: Eu^{2+} phosphors were mixed with epoxy resin in order to be pre-coated on the 370 nm LED chip. Another type of transparent epoxy resin was used to protect and fix the whole device, and the subsequent curing at 120 °C for 1 h by oven. The emission spectra of the fabricated LED were measured by PMS-50 LED spectrophotocolorimeter (EVERFINE, China).

3. Results and discussion

3.1. Crystal structure, phase identification

All the as-prepared $Sr_5(PO_4)_3F$: Eu^{2+} phosphors were collected to verify the phase purity by XRD. Fig. 1 shows the XRD patterns of $Sr_5(PO_4)_3F$ samples with different concentrations of Eu^{2+} ($0.004 \le x \le 0.016$). From Fig. 1, it can be seen that all the diffraction peaks agree well with that of the JCPDS standard pattern (PDF#50-1744), suggesting that the prepared samples belong to the pure phase and the doped ions has not brought about obvious changes in the phase structure. $Sr_5(PO_4)_3F$ crystallizes in a hexagonal system with space group $P_{63/m}$ (176). The corresponding lattice constants of the standard pattern are as follows: $a = b = 9.717$ Å, $c = 7.285$ Å, $Z = 2$ and $V = 595.8$ Å^3. $Sr_5(PO_4)_3F$ belongs to the apatite-type structure. Its crystal structure is shown in Fig. 2(a). We can see that the basic structural features of the $Sr_5(PO_4)_3F$ crystal include Sr^{2+} ions, F^- ions, and $(PO_4)^{3-}$ groups. As depicted in Fig. 2(b), there are two kinds of Sr^{2+} ions sites with different coordination environments in $Sr_5(PO_4)_3F$ lattice. One is the Wyckoff symbol 4*f* site coordinated by nine oxygen atoms, and the other is the 6*h* site coordinated by six oxygen atoms and one fluorine atom. We denoted as Sr1 and Sr2, respectively. Considering ionic charge and radius, Eu^{2+} ($r = 1.30$ Å when coordinate number (CN) = 9; $r = 1.20$ Å when CN = 7) should substitute the position of Sr^{2+} sites ($r = 1.36$ Å when CN = 9; $r = 1.21$ Å when CN = 7). Thus, the Eu^{2+}ions should enter into the Sr^{2+}ions sites in the $Sr_5(PO_4)_3F$ lattice. We predict that the Eu^{2+}ions randomly occupy the Sr^{2+} ions sites in the host lattice.

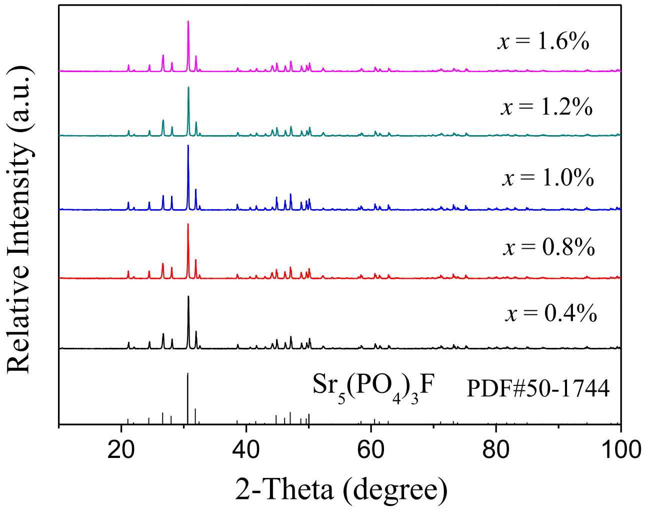

Fig. 1. XRD patterns of $Sr_{5(1-x)}(PO_4)_3F$: $5xEu^{2+}$ ($x = 0.004$–0.016) as well as the standard reference of the $Sr_5(PO_4)_3F$ compound (JCPDS card No. 50–1744).

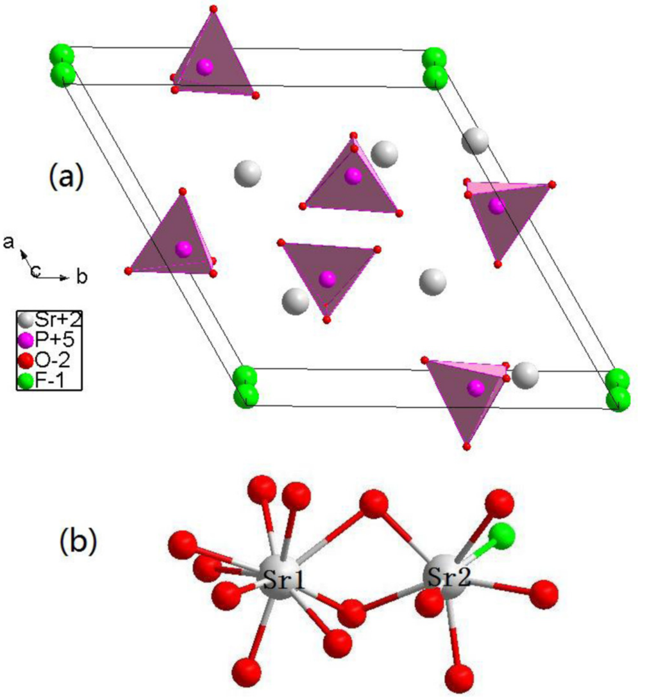

Fig. 2. (a) Crystal structures of $Sr_5(PO_4)_3F$ and (b) the coordination environment of the Sr.