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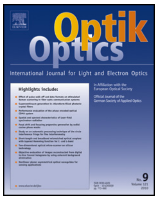

Original research article

Sm^{3+} doped $K_3Gd_3B_4O_{12}$: An orange-emitting phosphor for white light-emitting diodes

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ABSTRACT

$K_3Gd_{3-x}Sm_xB_4O_{12}$ orange phosphors were synthesized via the high temperature solid-state reaction method. The phase composition, morphology, particle size and luminescent properties were investigated using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectra (PL), respectively. The SEM images showed that the doped sample exhibited an irregular morphology with e diameter of about 2 μm. The optimum doping concentration was found to be 15 mol% for Sm^{3+} ion and the critical distance R_c was calculated to be 7.8846 Å. Under near-UV light (405 nm) excitation, they showed intense orange emission centered at 603 nm because of the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm^{3+} activator. Under 276 nm excitation, there existed a charge transfer from Gd^{3+} to Sm^{3+} and the charge transfer efficiency of $K_3Gd_{3-x}Sm_xB_4O_{12}$ can reach 99.88%. The CIE coordinates of phosphor $K_3Gd_{2.85}Sm_{0.15}B_4O_{12}$ are calculated to be (0.5895, 0.4096) and the color purity was estimated to be around 88%, which indicates that the phosphor may be potentially excited NUV chips for application in W-LEDs.

1. Introduction

In recent years, white light emitting diodes (W-LEDs) have attracted much attention due to the high stability, high brightness, long lifetimes, lower power consumption and environmental friendliness [1–4]. In general, there are two different methods to produce W-LEDs. On the one hand, the most commercially utilized kind of W-LEDs are produced by combining the blue LED chip with a yellow phosphor ($Y_3Al_5O_{12}$:Ce^{3+}), which mingles the blue light from the chip and yellow light from the phosphor resulting in white light. Whereas, this kind of white light has two disadvantages, such as, high corrected color temperature and poor color rendering index owing to the lack of red component, which severely limits further applications of yellow phosphor-based W-LEDs [5–7]. On the other hand, the W-LEDs can also be made by using a near-ultraviolet (NUV) LED to excite red, blue and green multiphase phosphors. So, red phosphor plays an important role in high quality W-LEDs. Hence, it is urgent for us to searching a excellent red-emitting phosphor which can be efficiently excited by NUV light.

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As is well-known, there are 17 chemical elements presenting singular properties, which resulted from their electronic configurations. The rare-earth ions have been investigated widely owing to the commercial applications for example high density frequency domain optical data storage, flat panel displays and solid lasers. As a kind of rare earth ions, Sm^{3+} ions are able to generate intense reddish orange emitting light since it can be excited to its $^4F_{7/2}$ energy level and then relaxed to the $^4G_{5/2}$ energy level through the non-radiative transition. Besides, Sm^{3+} ions have been known as major red-emitting sensitizers on some phosphors owing to the low cost. Above all Sm^{3+} ions have a high absorption coefficient around 404 nm and the main emission bands of $^7G_{5/2} \rightarrow {}^6H_{5/2,}$ $^7G_{5/2} \rightarrow {}^6H_{7/2}$, $^7G_{5/2} \rightarrow {}^6H_{9/2}$ and $^7G_{5/2} \rightarrow {}^6H_{11/2}$ fall in the visible range. To date, lots of orange-emitting phosphors have been investigated, such as $KBa_2(PO_3)_5$:Sm^{3+} [2], $K_4BaSi_3O_9$: Sm^{3+} [8], Gd_2MoO_6:Sm^{3+} [9], $BaMoO_4$:Sm^{3+} [10], etc.

Inorganic borates of luminescence materials have been used for preparing phosphors owing to their rich varieties in crystal structure, large band gap, environment friendliness, low synthesis temperature and high physical and chemical stability. Up till now, rare-earth activated borate based phosphors with good performance have been investigated, for example $Sr_3B_2O_6$:Ce^{3+},Eu^{2+} [11], $Sr_3Y_2(BO_3)_4$:Eu^{3+} [12], PbTbB7O13:Eu^{3+} [13], etc. It is reported that the borate of $K_3Y_3(BO_3)_4$ belongs to space group $P2_1/c$ with unit cell dimensions of a = 10.4667(16) Å, b = 17.361(3) Å, c = 13.781(2) Å and β = 110.548(8)°. The two compounds $K_3Y_3(BO_3)_4$ and $K_3Gd_3(BO_3)_4$ are isostructure and crystallize in a monoclinic space group $P2_1/c$ [14]. As everyone knows, the phosphor of $K_3Gd_{3\text{-}x}Sm_xB_4O_{12}$ has never been investigated so far. Hence, we report the synthesis, crystal structure, morphology and luminescent properties activated by Sm^{3+} for $K_3Gd_3B_4O_{12.}$

2. Experimental sections

2.1. Sample preparation

The $K_3Gd_{3\text{-}x}Sm_xB_4O_{12}$ (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15 and 0.20) phosphors were synthesized by the high temperature solid-state reaction method. The starting AR grade materials with 99.99% purity used for the preparation were potassium carbonate (K_2CO_3), gadolinium oxide (Gd_2O_3), boric acid (H_3BO_3) and samarium oxide (Sm_2O_3), which were purchased from Jiangxi Ganzhou Rare-Earth Limited Corporation. Stoichiometric amounts of K_2CO_3, Gd_2O_3, H_3BO_3 and Sm_2O_3 were blended and ground thoroughly in an agate mortar, and the homogeneous mixtures were preheated in alumina crucibles for 5 h at 600 ° to decompose K_2CO_3 and H_3BO_3. When cooling down to the room temperature, the presintered mixtures were ground and heated at 850 ° for 40 h, then cooling down to room temperature naturally, and then crushed to a fine powder for further measurements.

2.2. Measurements and characterization

The phase structure of the annealed $K_3Gd_{3\text{-}x}Sm_xB_4O_{12}$ phosphors was analyzed by X-ray powder diffraction performed on a Rigaku D/Max-RA X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm), operating at 40 kV and 150 mA; the scanning speed, step length and diffraction range were 10° min^{-1}, 0.05° and 5°–75°, respectively. The morphologies and sizes of the phosphors were observed using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi). Photoluminescence emission (PL) and photoluminescence excitation (PLE) spectrum of $K_3Gd_{3\text{-}x}Sm_xB_4O_{12}$ phosphors at room temperature were obtained on a fluorescence spectrophotometer (QM-4/2005SE, Photon Technology International Inc.) equipped with a 150 W Xe lamp as the excitation source, scanning at 1200 nm min^{-1}. The CIE coordinates were calculated by using the PL data according to the CIE 1931 standard colorimetric system. All the measurements were detected at room temperature.

3. Results and discussion

3.1. Structural analysis

As shown in Fig. 1, the XRD patterns of samples with 0–0.2 Sm^{3+} concentration were in good agreement with the calculated one. It can be clearly observed that all peaks can be well indexed to ICSD#160320 $K_3Y_3B_4O_{12}$ phase and there are no impurity phase was found in the phosphors when doping concentration in below 0.2. Hence, it can be concluded that the host crystal lattice are not changed by the Sm^{3+} ions dopant. Fig. 2(a) and (b) present the particle size and morphology of $K_3Gd_{2.85}Sm_{0.15}B_4O_{12}$ phosphor at different magnifications. From Fig. 2, it can be seen that the doped sample exhibit an irregular morphology with e diameter of about 2 μm.

3.2. Luminescent properties

Fig. 3 exhibits the photoluminescence excitation and emission spectra of $K_3Gd_3B_4O_{12}$ sample. As shown in Fig. 3, the excitation spectrum of the pure $K_3Gd_3B_4O_{12}$ sample monitored at 312 nm includes a sharp peak around 276 nm, attributing to the $^8S_{7/2} \rightarrow {}^6I_{7/2}$ transition of Gd^{3+} ion. Under 276 nm light excitation, the emission spectrum was recorded in the range of 300–400 nm, which presents a sharp emission band around 312 nm, corresponding to the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} ion.