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Luminescence properties of a novel red-emitting phosphor $LaBMO_6$: Pr^{3+} (M = W, Mo)

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ABSTRACT

A novel blue InGaN-chip-based red-emitting phosphor Pr^{3+}: $LaBMO_6$ (M = W, Mo) in pure phase were synthesized via conventional solid-state reaction in air and the photoluminescence properties of the phosphor were investigated for the application in white LEDs. The as-synthesized phosphors were characterized by the X-ray diffraction; diffuse reflection spectra, photoluminescence excitation and emission spectra, the Commission International de L'Eclairage (CIE) chromaticity coordinates and temperature-dependent emission spectra. Orangish red emission band around 575–625 nm was observed in Pr^{3+}-doped $LaBMO_6$ (M = W, Mo) upon 445 nm excitation. Fluorescence concentration quenching in Pr^{3+}-doped $LaBMoO_6$ were observed and the critical distance between Pr^{3+} ions for energy transfer was calculated to be 8.369 nm. The CIE chromaticity coordinates of Pr^{3+}-doped $LaBMoO_6$ were located in the red spectral region and the temperature-dependent luminescence spectra indicated that Pr^{3+}-doped $LaBMoO_6$ show good thermal stability. All results demonstrated the developed Pr^{3+}-doped $LaBMO_6$ (M = W, Mo) was a novel red phosphor.

1. Introduction

White light-emitting diodes (LEDs) are presumed to be next generation solid-state lighting devices because of their outstanding characteristics such as high luminous efficiency, less energy consumption, long lifetime and environment-friendliness [1–3]. Recently, white LEDs can save approximately 70% of the energy used for incandescent light bulbs. The most convenient and dominant way of making white LEDs are based on the combination of a blue InGaN LED chip (440–470 nm) and yellow-emitting phosphor YAG: Ce^{3+} due to their simpler and more cost effective fabrication [4]. However, these white LEDs have several serious drawbacks such as low color-rendering index, high correlated color temperature because of the lack of color in the red region, low thermal quenching temperature and narrow visible range [5]. Therefore there are two approaches to overcome those problems, one is a combination of an ultraviolet (UV) LED chip and tri-color phosphors; the other is to propose a blue LED chip with green and red phosphors [6]. Consequently, red phosphors with broadband absorption in the blue range have attracted substantial attentions.

In recent year, the most successful materials used for red phosphors are Eu^{2+}-, Eu^{3+}-or Mn^{4+}-doped (oxy)nitride compounds [7–15]. Typical $CaAlSiN_3$:Eu^{2+} phosphors commercialized by Albeit have some drawbacks such as broadband emission beyond 650 nm, server re-absorption and rigorous synthesis conditions [8]. $Sr[LiAl_3N_4]$:Eu^{2+} has been reported to be promising narrow-band red-emitting phosphors excited by GaN-based LEDs [9]. Eu^{3+}-doped oxides, vanadate have been investigated as near-UV-excited red-emitting phosphors for lighting and displays [10–12]. Mn^{4+}-activated fluoride compounds as red-emitting phosphors have been reported to be successfully synthesized by cation exchange reaction, and the Mn^{4+}-based white LED with low color temperature and high color-rendering index have been obtained [13]. Recently, other Mn^{4+}-activated fluorides as red phosphors have been widely researched [14,15]. However, those fluoride or nitride compounds are poorly stable and inefficient at high temperature. Comparatively, Pr^{3+} ions can exhibit prominent red luminescence in some oxide-based compounds upon UV or blue

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photon excitation because of the quenching of $^3P_0$ emission [16–20]. A highly stable red-emitting phosphor β-SiAlON:Pr^{3+} has been proved to be a promising phosphor applied in white LED [17]. Pr^{3+}-doped $Sr_2Al_2SiO_7$ has been investigated as thermal-stable red phosphor for blue LED [18].

$LaBMO_6$ (M = W, Mo) is a member of the molybdenum borate family with a general formula $LnBMO_6$ (Ln = La-Nd, and M = W, Mo) [21,22]. Yu et al. have reported that the Mo atoms are bound to five O atoms by strong distorted trigonal-bipyramidal coordination [21]. Sm^{3+}-, Dy^{3+}-doped boro-molybdates phosphors have been investigated by Zhang et al. to be promising luminescent materials [23]. Zhu et al. have reported Sm^{3+}-, Dy^{3+}-doped $LaBWO_6$ as potential materials in luminescent display applications [24]. Recently, Eu^{3+}-doped boro-tungstates have been paid more attention as candidates for red-emitting phosphors in white LEDs [25–27]. Eu^{3+}-doped $LaBWO_6$ nano-phosphors have been demonstrated to be red phosphors applied in white LEDs [26]. $LaBMoO_6$: Eu^{3+} has been reported to be near-UV-based color-conversion red phosphor [27]. Therefore, the Eu^{3+}-doped boro-molybdate or tungstate compounds are potential red-emitting phosphors for solid-state lighting based on near-UV or blue LED chips.

To the best of our knowledge, Pr^{3+}-doped boro-molybdate or tungstate compounds as red phosphors suitable for the commercial blue LED excitation have not been reported. In this work a novel red-emitting phosphor Pr^{3+}-doped $LaBMO_6$ (M = W, Mo) was prepared by high-temperature solid-state reaction and luminescent properties were investigated in detail. Fluorescence concentration quenching in Pr^{3+}:$LaBMO_6$ (M = W, Mo) and thermal stability of this phosphor were also researched.

2. Experiments

The Pr^{3+}-doped $LaBMO_6$ (M = W, Mo) phosphors formulated $La_{1-x}Pr_xBMO_6$ (x = 0–0.10, M = W, Mo) were synthesized by solid-state reaction method at high temperature. Raw materials La_2O_3 (99.99%), H_3BO_3 (analytical reagent), WO_3 (analytical reagent), MoO_3 (analytical reagent) and Pr_6O_{11} (99.99%) were obtained from Sinopharm Chemical Reagent, Co. Ltd, China and used as received without further purification. Firstly stoichiometric amounts of all the above reagents were weighed according to the composition of $La_{1-x}Pr_xBMoO_6$ (x = 0, 0.001, 0.003, 0.005, 0.01, 0.02, 0.04, 0.08 and 0.10) or $La_{1-x}Pr_xBWO_6$ (x = 0, 0.005, 0.01, 0.02, and 0.04). Additional 10.0 at.% H_3BO_3 was used to compensate the losses due to evaporation during the synthesis process. Then the weighted materials were mixed thoroughly in an agate mortar for 30 min, and transferred to a corundum crucible and pre-sintered at 300 °C for 2 h in a muffle furnace. Finally, the calcined powders were reground and re-sintered at 950 °C for 8 h in air. After being cooled to room temperature naturally, the obtained samples were reground into powder for further characterization.

The structure of the as-synthesized phosphors were investigated by an X-ray powder diffraction (XRD) diffractometer (X'pert pro X-ray diffractometer, Panalytical Co.) with Cu Ka radiation (λ = 0.15418 nm) at 40 K*V* tube voltage and 40 m*A* tube current. The patterns in 2θ were from 10° to 80° with about 2 (°)/min speed. Diffuse reflectance spectra were recorded by a spectrophotometer (Lambda 650S, Perkin Elmer Co.). $BaSO_4$ was used as a reference for 100% reflectance during the measurement. Photoluminescence (PL) emission and excitation spectra of the phosphors were measured using a fluorescence spectrophotometer (Cary Eclipse, Agilent Technologies Co.). For each PL emission and excitation measurement, the fluorescence signals were detected with the 1.0 nm excitation and emission slit widths. The Commission International de L'Eclairage (CIE) 1931 chromaticity coordinates of all the phosphors were obtained by a color analyzer equipped with a CCD detector (HAAS-2000, Yuanfang, Hangzhou, China). Absolute photoluminescence quantum efficiency was measured using an absolute PL quantum yield measurement system C9920-02 (Hamamatsu Co., Japan). All the above measurements were carried out at room temperature. The temperature-dependence luminescence spectra of the phosphor were recorded by using a thermal quenching analyzer for phosphors (EX-1000, Yuanfang, Hangzhou, China).

3. Results and discussion

Crystal structure of $LaBMoO_6$ compound has been investigated recently, and it is a monoclinic space group $P2_1/c$ with the lattice parameters: a = 10.2968(8)Å, b = 4.1636(3)Å, and c = 23.8587(5)Å, [28]. $LaBWO_6$ crystallizes in the orthorhombic system with the space group of $P222$ and cell parameters of a = 0.410 Å, b = 1.031 Å, c = 2.171 Å [29]. To check the phase purity of the as-synthesized samples, XRD patterns of all phosphors were recorded. Some typical XRD patterns of $La_{1-x}BWO_6$: xPr^{3+} (x = 0, 0.005, 0.01, and 0.04) phosphors are shown in Fig. 1(a). The XRD results shown in Fig. 1(a) mean that all the diffraction peaks of Pr^{3+}-doped $LaBWO_6$ phosphors with different Pr^{3+} concentrations were consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) card No. 35-0216 and the previous reported patterns [24,25]. Fig. 1(b) shows typical XRD patterns of $La_{1-x}BMoO_6$: xPr^{3+} (x = 0, 0.08, and

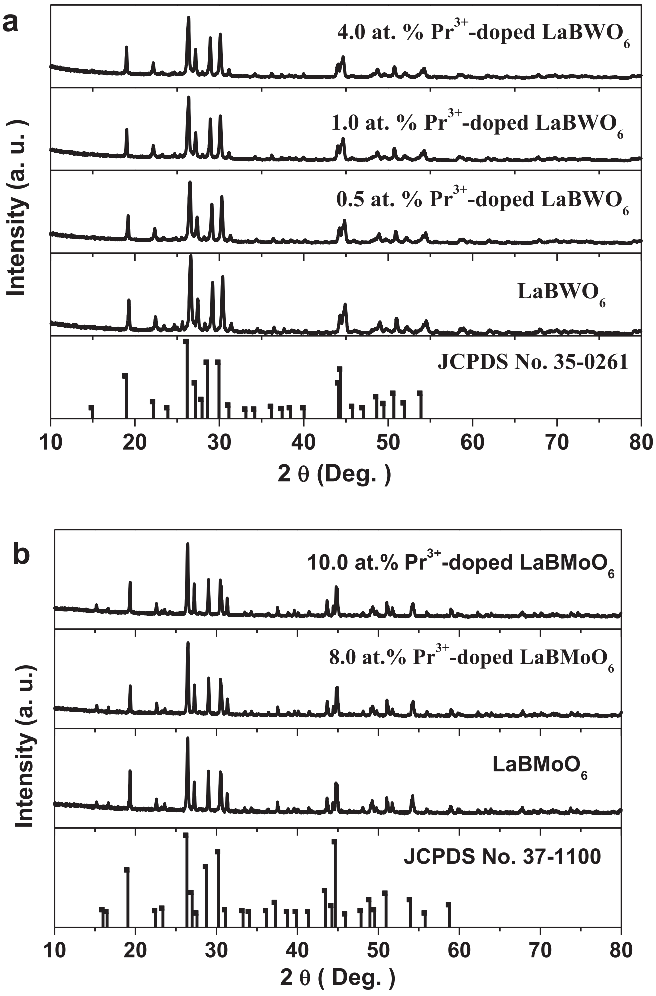

Fig. 1. X-ray powder diffraction patterns of $La_{1-x}BWO_6$: xPr^{3+} (x = 0, 0.005, 0.01, and 0.04) phosphors (a) and $La_{1-x}BMoO_6$: xPr^{3+} (x = 0, 0.08, and 0.10) phosphor (b).