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A novel white-light-emission phosphor Dy^{3+}-doped $CaLaB_7O_{13}$ under UV excitation

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ABSTRACT

White-light-emitting phosphors Dy^{3+}-doped $CaLaB_7O_{13}$ were synthesized by solid-state reaction, and their luminescent properties were characterized for the applications in white-light-diodes (W-LEDs). The obtained samples were initially investigated by X-ray powder diffraction, photoluminescence excitation and emission spectra, the Commission International de L'Eclairage (CIE) chromaticity coordinates, and thermally stable properties. Dy^{3+}-doped $CaLaB_7O_{13}$ phosphors emitted a blue emission band centered at 480 nm and a yellow one centered at 575 nm with CIE chromaticity coordinates of (0.325, 0.339) under the excitation of near-UV (NUV) LED chips at 365 nm. The electric dipole-dipole interaction was demonstrated to be the energy transfer mechanism in Dy^{3+}-doped $CaLaB_7O_{13}$ phosphors, and the critical distance of energy transfer between the Dy^{3+} ions was estimated to be about 0.920 nm. The temperature-dependent spectra imply Dy^{3+}-doped $CaLaB_7O_{13}$ show small thermal quenching. The present work indicated that Dy^{3+}-doped $CaLaB_7O_{13}$ was a promising white-light-emitting phosphor excited by NUV LED.

1. Introduction

Solid-state lighting have attracted a sea of attention recently becomes a smart strategy for energy saving, safety, reliability and eco-friendly characteristics [1,2], and white light-emitting diodes (W-LEDs) are believed as the most promising illumination technology in solid-state lighting industries [3,4]. At present, there are two general approaches to obtain W-LEDs: one is packing red, green and blue LED chips together to produce white light, and the other is combining fluorescent phosphors with a LED chip. Currently the commercial W-LEDs are mainly obtained by combining a 460 nm blue-emitting GaN chip with yellow emitting yttrium aluminum garnet (YAG) phosphor doped Ce^{3+} because of simple fabrication and mature processing. However, this type of W-LEDs have some drawbacks such as poor color rendering index (CRI) and high correlated color temperature (CCT) due to lacking a red component [5]. Therefore, W-LEDs based on near ultraviolet (UV) LED chips and tri-colors (RGB) phosphors have been proposed, and high-performance blue, green and red phosphors suitable to be excited by near UV LED light have attracted much attention in recent years [6,7].

Dy^{3+}-doped phosphors have received lots of attentions among the W-LEDs researches [8–17], because there are two characteristic emission bands. One emission band is the blue one centered at 480 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and the other is an intense yellow one centered at 575 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$). The ratio of two dominant Dy^{3+} emission bands is tunable with different dopant concentrations, host compositions and excitation wavelengths [13,14]. It is well-known that the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ magnetic dipole transition is stronger when Dy^{3+} located at around high symmetry crystal field, while the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ electric dipole transition is prominent when Dy^{3+} located at low symmetry site without an inversion center. As a result it is possible to obtain white light emission in Dy^{3+}-single-doped phosphors. Compared with other method such as combining RGB phosphors with near UV LED chips which intensive reabsorption of different phosphors exists, the method of Dy^{3+}-single-doped phosphor with UV excitation is more efficient [15]. Therefore, many host crystals that can be activated by Dy^{3+} ions have been intense studied, such as vanadates [16], silicates [14,17], borates [8,18], molybdates [19], tungstates [10,11], aluminates [20] and fluorides [21].

Borates are excellent host lattices for luminescent materials because of their wide UV transparency, high optical damage threshold, and good chemical stability [22]. Eu^{3+}, Tb^{3+} or Ce^{3+}-doped $CaLaB_7O_{13}$ have been obtained and presented red, green or violet fluorescence respectively [23]. Recently, Dy^{3+}-doped

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Ca_3Si_2O7 phosphors with various Dy^{3+} concentrations were obtained and the color coordinates of the phosphors was within the white light region through varying the Dy^{3+} concentration under 350 nm excitation [24]. Dy^{3+}, Eu^{3+}-codoped $LiInW_2O_8$ phosphors show a white emission under the host excitation [11,25]. However, to the best of our knowledge, there were little or no report on Dy^{3+}-doped $CaLaB_7O_{13}$ as white-light-emitting phosphor applied in W-LEDs. Inspired by the exploration of thermal-stable phosphor for high power W-LED, in this work the luminescent properties of Dy^{3+}-doped $CaLaB_7O_{13}$ were extensively investigated and thermal stability properties of these phosphors were also discussed.

2. Experiments

All the phosphors were characterized by powder X-ray diffraction (XRD) using a Panalytical X'pert pro X-ray diffractometer with Cu Ka source ($\lambda = 0.15418$ nm) operating at 40 kV and 40 mA with the scan range from 10° to 90° at about 2 (°)/min speed. Diffuse reflectance spectra were recorded using a Lambda 650S (Perkin Elmer Co.) spectrophotometer. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded on a Cary Eclipse (Agilent Technologies Co.) fluorescence spectrophotometer. During each PL emission and PLE measurement, fluorescent signals from the phosphors in a quartz holder were detected with the same excitation and emission slit widths in the spectrophotometer. The slits for both excitation and emission were set as 2.0 nm and the scanning speed was fixed at 200 nm min^{-1}. Photoluminescence quantum yield was measured by absolute PL quantum yield measurement system C9920-02 (Hamamatsu Co., Japan). CIE 1931 chromaticity coordinates and CCT of all the phosphors were obtained by a HAAS-2000 color analyzer equipped with a CCD detector (Yuanfang, Hangzhou, China). The temperature-dependence luminescence spectra of the phosphor were recorded by using an EX-1000 thermal quenching analyzer for phosphors (Yuanfang, Hangzhou, China). All the measurements except for the temperature-dependence spectra were carried out at room temperature.

A series of $CaLa_{1-x}B_7O_{13}$: xDy^{3+} ($x = 0$, 0.005, 0.01, 0.02, 0.04, 0.06 0.08, 0.10 and 0.15) phosphors were synthesized by traditional solid-state reaction method. Stoichiometric amount of raw materials $CaCO_3$ (analytical reagent), H_3BO_3 (analytical reagent), La_2O_3 (99.99%) and Dy_2O_3 (99.99%) were weighed according to the nominal compositions of $CaDy_xLa_{1-x}B_7O_{13}$ ($x = 0$–0.15), and thoroughly ground in an agate mortar for 20 min. Then the homogeneous mixtures were filled into alumina crucible and sintered at 900 °C for 10 h in air. After being cooled to room temperature naturally, the final products were reground to powder for measurement.

3. Results and discussion

XRD patterns of all phosphors were recorded and several typical XRD patterns of $CaLa_{1-x}B_7O_{13}$: xDy^{3+} ($x = 0$, 0.005 and 0.15) are shown in Fig. 1. It was obvious that the position and relative intensity of the diffraction peaks of all samples were almost consistent with the standard Joint Committee on Powder Diffraction Standards (JCPDS) cards No. 44-0353, corresponding to the intrinsic diffraction patterns of pure $CaLaB_7O_{13}$. No impurity lines were observed in those figures even for the 15.0 at.% Dy^{3+}-doped sample. Crystal structure of $CaLaB_7O_{13}$ was firstly investigated in 1990 s, and it is a monoclinic structure with $a = 11.018$ Å, $b = 6.545$ Å, $c = 9.091$ Å, $\beta = 91.51°$ and $Z = 3$ [23]. Because the Dy^{3+} and La^{3+} ions have almost the same ion radii for lanthanide contraction, it was expected that the Dy^{3+} ions can be mostly incorporated into the sites of La^{3+} ions and the dopants did not change the crystal structure.

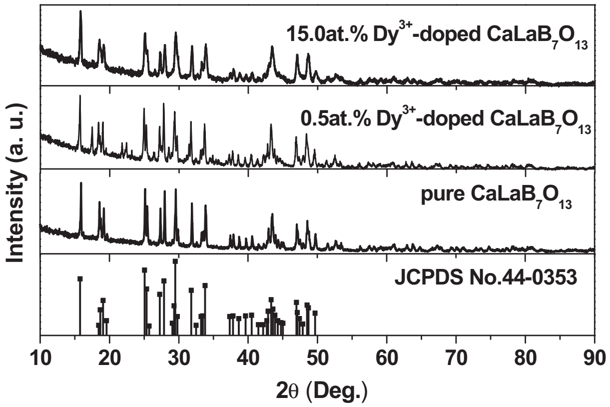

Fig. 1. X-ray powder diffraction patterns of $CaLa_{1-x}B_7O_{13}$: xDy^{3+} ($x = 0$, 0.005 and 0.15) phosphors.

The ultraviolent-visible (UV–Vis) reflectance spectra of the obtained phosphors were recorded by an integrating sphere. All reflectance spectra were similar and two typical spectra of the host $CaLaB_7O_{13}$ and 8.0 at.% samples were shown in Fig. 2. The inset in this figure was the enlargement of absorption bands of the Dy^{3+} ions transitions in the 8.0 at.% sample. The bands around 380, 420, 440 and 460 nm were assigned to the transitions of Dy^{3+} from the ground $^6H_{15/2}$ manifolds to the excited $^4I_{13/2}$, $^4G_{11/2}$, $^6H_{11/2}$ and $^6F_{9/2}$ manifolds respectively [26]. It was evident that for the $CaLaB_7O_{13}$ host the transmittance efficiency within the visible spectral range remain more than 80% and high transmittance efficiency in the visible spectral rang mean this host was suitable for the applications in W-LEDs.

The PL emission and PLE spectra of 8.0 at.% Dy^{3+}-doped $CaLaB_7O_{13}$ were presented in Fig. 3. The PLE spectra (black solid line) were monitored at 575 nm, corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} ions. As shown in those figures, there were some strong excitation bands in this spectrum within the range of 320–450 nm which were due to the $4f^9 \rightarrow 4f^9$ transitions of the Dy^{3+} ions, and the main excitation band centered at 325, 350, 365, 385, 420 and 450 nm corresponded to the $^6H_{15/2} \rightarrow {}^6P_{3/2}$,

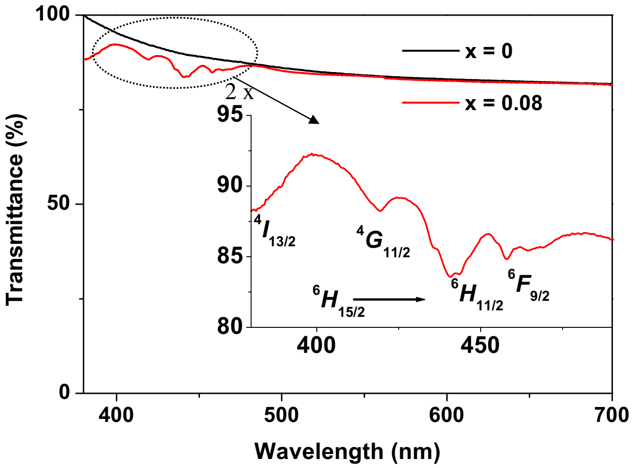

Fig. 2. The ultraviolent-visible diffuse reflectance spectra of $CaLaB_7O_{13}$ (black solid curves) and $CaLa_{1-x}B_7O_{13}$: xDy^{3+} ($x = 0.08$) phosphor (red solid curves), and the inset show enlargement of several absorption bands of the Dy^{3+} ions in 8.0 at.% Dy^{3+}-doped $CaLaB_7O_{13.}$ (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)