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Synthesis and photoluminescence properties of near-UV pumped yellow-emitting $Li_3Ba_2La_3(WO_4)_8:Dy^{3+}$ phosphors

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ABSTRACT

$Li_3Ba_2La_3(WO_4)_8:Dy^{3+}$ yellow-emitting phosphors were synthesized by the solid state reaction method. These phosphors exhibit one intense emission band around 575 nm under excitation at 365 nm. The dependences of the emission intensities and the chromaticity coordinates on Dy^{3+} concentration were analyzed. The optimum doping concentration of Dy^{3+} for the phosphor is about 6 mol% and the corresponding chromaticity coordinates is (0.435, 0.476) at room temperature. Besides, the $Li_3Ba_2La_3(WO_4)_8:Dy^{3+}$ phosphor shows higher thermal stability than that of $(Sr, Ba)_2SiO_4:Eu^{2+}$. The results show that the $Li_3Ba_2La_3(WO_4)_8:Dy^{3+}$ phosphor with strong yellow emission may be applied in near ultraviolet pumped white LEDs.

1. Introduction

In recent years, white light sources based on near ultraviolet LEDs (near-UV LEDs, 350–410 nm) have attracted interest. Compared with the white-LEDs combining a blue InGaN chip and yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ ($YAG:Ce^{3+}$) phosphor [1,2], they have higher color-rendering properties and their color temperatures can be tuned by changing the red/green/blue (R/G/B) or yellow/blue (Y/B) ratios [3–5].

Dy^{3+} is a preferred active ion for phosphors because it can be excited by commercial near-UV LEDs [6–8]. The ion has two intense emission bands in blue and yellow regions related with the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively. The $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is a hypersensitive transition and strongly influenced by the crystal field [9]. Therefore, it is possible to adjust the intensity ratio of yellow to blue emission via choosing different hosts. These two 4*f*–4*f* transitions of Dy^{3+} are electronic dipole forbidden, so the intensities of these emissions are weaker than those of the electronic dipole permissible 4*f*–5*d* transitions of Eu^{2+} and Ce^{3+} [10,11]. An approach for improving the brightness of Dy^{3+}-doped phosphor is increasing the concentration of Dy^{3+} without fluorescence quenching [12]. For example, the $NaY(WO_4)_2:Eu^{3+}$ and $Li_3Ba_2Gd_3(MoO_4)_8:Eu^{3+}$ red phosphors with high concentration of Eu^{3+} have high brightness of red emission [13,14].

Recently, ternary molybdates $Li_3Ba_2Ln_3(MoO_4)_8$ (Ln = La–Lu, Y) with space group C2/c and $Z = 2$ have been studied as hosts of potential white LEDs phosphors, such as the $Li_3Ba_2Gd_3(MoO_4)_8:Eu^{3+}$ and $Li_3Ba_2Y_3(MoO_4)_8:Dy^{3+}$ [12,14]. The tungstate $Li_3Ba_2La_3(WO_4)_8$ (LBLW), which is isostructural with the $Li_3Ba_2Ln_3(MoO_4)_8$, has been investigated as a host for solid-state laser, and its crystal structure has been solved by Pan et al. [15,16]. The average distance of La–La in LBLW is up to 3.78 Å, which is longer than the 3.70 Å of Gd–Gd in $Li_3Ba_2Gd_3(MoO_4)_8$ and the 3.68 Å of Y–Y in $Li_3Ba_2Y_3(MoO_4)_8$ [12,14]. The longer distance between rare earth ions in LBLW would be beneficial to reducing the concentration dependent fluorescence quenching. Therefore, the LBLW may also be a suitable host for a bright phosphor with high Dy^{3+} doping.

In this work, $LBLW:Dy^{3+}$ phosphors with different concentrations of Dy^{3+} were synthesized by the solid state reaction method. The photoluminescence (PL) properties of the $LBLW:Dy^{3+}$ phosphors and the effects of Dy^{3+} concentration on the PL properties were investigated in detail. The chromatic properties of the phosphors were also analyzed.

2. Experimental procedure

2.1. Material and synthesis

A series of powder samples $Li_3Ba_2La_{3(1-x)}Dy_{3x}(WO_4)_8$ ($LBLW:xDy^{3+}$) with different Dy^{3+} concentrations ($x = 0$, 0.005, 0.02, 0.04, 0.06, 0.08, and 0.1) were prepared by the solid state reaction method. The raw materials were Li_2CO_3 (A.R. (Analytical

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Reagent)), $BaCO_3$ (A.R.), La_2O_3 (99.99%), WO_3 (A.R.), and Dy_2O_3 (99.99%). The stoichiometric amount of raw materials was thoroughly mixed by ground in an agate mortar. The mixtures of starting materials were then transferred to crucibles and had been subsequently heated at 900 °C for 24 h in air atmosphere. As the muffle furnace cooled to room temperature naturally, the final products were collected and ground to powder for further characterization.

2.2. Measurements and characterization

Phase purity of the synthesized powders was checked by the X-ray powder diffraction (XRD), which was carried out in an angular range $15° < 2\theta < 65°$ using Ni-filtered Cu Kα radiation on a Rigaku MiniFlex II diffractometer working in Bragg–Brentano ($\theta/2\theta$) geometry. For the refinement of the crystal structure for LBLW:Dy^{3+}, lattice parameters were calculated using a profile fitting by a least-squares method (Rietveld method) employing the computer program GSAS implemented with EXPGUI in which Ni powders served as an internal standard for peak position calibration [17].

UV–Vis absorption spectra were recorded using a spectrophotometer (Lambda900, Perkin-Elmer) in a range of 300–550 nm. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra in a range of 230–500 nm and 400–800 nm, respectively, were measured using a spectrometer (FL920, Edinburgh) equipped with a xenon lamp as the exciting source and a Hamamatsu R955 photomultiplier tube (PMT) as the detector. Fluorescence decay curves of the $^4F_{9/2}$ multiplet were measured by another spectrometer (FLSP920, Edinburgh) equipped with a tunable mid-band optical parametric oscillator pulsed laser (∼5 ns) (Vibrant355II, OPOTEK) as the exciting source and a Hamamatsu R955 PMT as the detector.

3. Results and discussion

3.1. Phase identification of LBLW:Dy^{3+} phosphors

All peaks of the XRD for the synthesized samples matched well with the XRD pattern for pure LBLW, which was calculated by Diamond program from the crystal parameters of LBLW, while no other peaks can be observed [15]. For brevity, XRD patterns of some samples LBLW:$x$$Dy^{3+}$ (x = 0, 0.02, 0.06, 0.1) and the calculated XRD pattern of LBLW are shown in Fig. 1(a). Rietveld refinement of the powder XRD pattern of LBLW:$x$$Dy^{3+}$ (x = 0, 0.1) was performed to investigate the change of unit cell parameters after doped with Dy^{3+} ions. Fig. 1(b) shows the observed (crosses) XRD pattern of LBLW: $x$$Dy^{3+}$ (x = 0, 0.1) and fitted (solid line) XRD pattern as well as the differences between them (bottom). The refined crystallographic data of LBLW:$x$$Dy^{3+}$ (x = 0, 0.1) are summarized in Table 1 [15]. The obtained fitting parameters $R_p = 13\%$, $R_{wp} = 12\%$, and $\chi^2 = 2.40$ for pure LBLW, and $R_p = 8\%$, $R_{wp} = 11\%$, and $\chi^2 = 2.45$ for LBLW:0.1Dy^{3+} demonstrate the phase purity of the samples. Furthermore, based on the effective ionic radii of cations reported by Shannon, the Dy^{3+} ions are expected to occupy La^{3+} sites and Ba^{2+} sites with charge compensation randomly [6,18]. As the ionic radius of Dy^{3+} is smaller than La^{3+} and Ba^{2+} (Dy^{3+}:0.91 Å, La^{3+}:1.06 Å, Ba^{2+}:1.35 Å), the lattice constants a, b, and c, and the unit cell volume of the LBLW:0.1Dy^{3+} are smaller than those of the pure LBLW as shown in Table 1.

3.2. Photoluminescence properties of LBLW:Dy^{3+}

Fig. 2(a) shows the UV–Vis absorption spectrum of the LBLW:0.1Dy^{3+}. The spectrum shows that the LBLW host exhibits an absorption band at wavelength shorter than 320 nm, which is due to the charge transfer band (CTB) of $(WO_4)^{2-}$ groups [19]. The sharp peaks in the range from 320 to 460 nm are related to the typical intra-4f transitions of Dy^{3+} ions.

The PLE spectrum of LBLW:0.1Dy^{3+} monitored at 575 nm emission ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) is shown in Fig. 2(b). The broad excitation band in the UV region from 210 to 310 nm is mainly ascribed to the CTB of $(WO_4)^{2-}$ groups, which indicates the existence of energy transfer from $(WO_4)^{2-}$ groups to Dy^{3+} ions in the LBLW:Dy^{3+} phosphors. The other part is a series of narrow excitation bands centered at 326, 352, 365, 387, 427, 453, and 475 nm, which are attributed to the intra-4f transitions of the Dy^{3+} ions, i.e., $^6H_{15/2} \rightarrow {}^6P_{3/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4M_{21/2}$, $^4G_{11/2}$, $^4I_{15/2}$, and $^4F_{9/2}$, respectively. The excitation bands at 350–400 nm indicate that the LBLW:Dy^{3+} phosphor is suitable to be excited by near-UV LEDs.

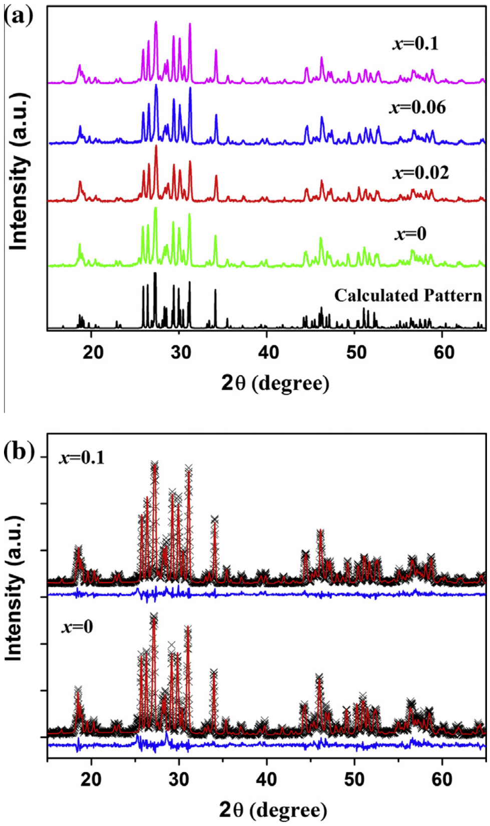

Fig. 1. (a) XRD patterns of LBLW:$x$$Dy^{3+}$ (x = 0, 0.02, 0.06, 0.1). (b) The experimental (crosses) and calculated (solid line) XRD patterns of LBLW:xDy^{3+} (x = 0, 0.1), and difference (bottom line) between them.

Table 1
Refined parameters of LBLW:$x$$Dy^{3+}$ (x = 0, 0.1) and crystal parameters of LBLW.

Formula	LBLW:0.1Dy^{3+}	LBLW[b]	LBLW[a]
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C_{2/c}$ (No. 15)	$C_{2/c}$ (No. 15)	$C_{2/c}$ (No. 15)
a (Å)	5.300	5.314	5.323
b (Å)	12.992	13.048	13.091
c (Å)	19.40	19.45	19.48
β (°)	91.43	91.36	91.18
Volume (Å^3)	1336	1347	1357
Z	2	2	2
R_p	0.08	0.13	
R_{wp}	0.11	0.12	
χ^2	2.45	2.40	

[a] The crystal parameters of LBLW from Ref. [14].
[b] The pure LBLW phosphor synthesized in this work.