Materials Letters 181 (2016) 305–308

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

$Ce^{3+} \rightarrow Tb^{3+}$ energy transfer induced emission-tunable properties of $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$ phosphors

Bing Han [a,*], Jingtao Zhang [b], Bingkun Liu [a], Jie Zhang [a], Hengzhen Shi [a,*]

[a] School of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, People's Republic of China
[b] School of Food and Bioengineering, Zhengzhou University of Light Industry, Zhengzhou 450002, People's Republic of China

ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form
12 June 2016
Accepted 13 June 2016
Available online 15 June 2016

Keywords:
Phosphors
$Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$
Energy transfer
Color-tunable
Luminescence

ABSTRACT

A series of Ce^{3+}/Tb^{3+} co-doped $Ba_3La(PO_4)_3$ phosphors were synthesized successfully via a high-temperature solid-state reaction, and their luminescence properties were investigated. The energy transfer phenomenon of $Ce^{3+} \rightarrow Tb^{3+}$ in $Ba_3La(PO_4)_3$ host was authenticated by relevant excitation spectra and decay curves, which leads to the change of luminous color for $Ba_3La(PO_4)_3:Ce^{3+}$, Tb^{3+} phosphors by tuning the quantity ratio of Ce^{3+} and Tb^{3+}. Meanwhile, the $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer efficiencies were also calculated in this system. These results suggest that as-developed $Ba_3La(PO_4)_3:Ce^{3+}$, Tb^{3+} phosphors are potential single-component color-tunable phosphors.

1. Introduction

$Ce^{3+} \rightarrow Tb^{3+}$ energy transfer (ET) is an important optical phenomenon for luminescence materials, which have been investigated deeply over the past years due to its potential application in display and lighting region [1–6]. Generally speaking, there are two main purposes on utilizing $Ce^{3+} \rightarrow Tb^{3+}$ ET in phosphors. (1) To enhance the green emission of Tb^{3+} under ultraviolet (UV) excitation [5]. A typical sample, $LaPO_4:Ce^{3+},Tb^{3+}$, as a famous green light emitting phosphor, has been applied in lamp industry for many years. (2) To realize the emission-tunable properties in visible region in a single-component phosphor under near-UV excitation [7–11]. Obviously, the latter one is research hotspot nowadays because of its application prospect in white light-emitting diodes (w-LEDs), which is considered as an ideal candidate for the replacement of conventional lighting resource [3,9]. So the investigation on the $Ce^{3+} \rightarrow Tb^{3+}$ ET in novel host is indispensable in order to develop proper single-component color-tunable phosphor for practical industrial applications.

An eulytite-type of orthophosphate, $Ba_3La(PO_4)_3$ [12], is an important host material for luminescence of rare-earth metal ions and transition metal ions. Many research groups have given considerable attention to the luminescence properties of $Ba_3La(PO_4)_3$-based phosphors for potential application in display and lighting regions [13–18]. The related published studies were grouped mainly on two categories, according to the research contents: (1) Spectroscopic properties of $Ba_3La(PO_4)_3$ doped with a single activator, e.g. $Ba_3La(PO_4)_3:Eu^{3+}$ [13], $Ba_3La(PO_4)_3:Sm^{3+}$[14]; (2) ET process among different activators in $Ba_3La(PO_4)_3$ host, e.g. $Gd^{3+} \rightarrow Tb^{3+}$ [15], $Gd^{3+} \rightarrow Dy^{3+}$ [16], $Tb^{3+} \rightarrow Eu^{3+}$[17], and $Eu^{2+} \rightarrow Mn^{2+}$[18]. However, to our knowledge, there is no report on the luminescence and ET of Ce^{3+}/Tb^{3+} co-doped $Ba_3La(PO_4)_3$ phosphors. So, in this work, a series of emission-tunable $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$ phosphors were synthesized via a high-temperature solid-state reaction, and their luminescence properties were investigated in detail.

2. Experimental

A series of $Ba_3La_{0.92-x}Tb_xCe_{0.08}(PO_4)_3$ ($x=0$, 0.01, 0.03, 0.05, 0.1, 0.2, and 0.3) phosphors and a Tb^{3+} single-doped sample $Ba_3La_{0.9}Tb_{0.1}(PO_4)_3$ were synthesized by a solid state reaction at high temperature. The starting materials are $BaCO_3$ (A.R.), $NH_4H_2PO_4$ (A.R.), La_2O_3 (99.99%), CeO_2 (99.99%), and Tb_4O_7 (99.99%), which were weighed in stoichiometric amounts and thoroughly mixed by grinding in an agate mortar. Then the mixtures were pre-fired at 600 °C for 2 h and sintered at 1250 °C for 6 h under a CO reducing atmosphere. Finally, the as-prepared phosphors were cooled to room temperature and reground into pulverous samples for further measurements.

---

* Corresponding auhor.
E-mail addresses: hanbing@zzuli.edu.cn (B. Han), shihz@zzuli.edu.cn (H. Shi).

http://dx.doi.org/10.1016/j.matlet.2016.06.061
0167-577X/

The crystalline phases of the final products were characterized by a powder X-ray diffraction (XRD) analysis with Cu Kα (λ=1.5405 Å) radiation on a Bruker D8 Advance X-Ray Diffractometer. Photoluminescence (PL) spectra and decay curves were recorded using an FLS980-Combined Fluorescence Lifetime & Steady State Fluorescence Spectrometer (EDINBURGH INSTRUMENTS) with a 450 W xenon lamp and a Picosecond Pulsed Light Emitting Diode (EPLED-250) with an excitation wavelength 251.6 nm as the excitation source, respectively. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the comparison of powder XRD patterns of singly and doubly doped samples $Ba_3La(PO_4)_3:Ce^{3+}$, $Ba_3La(PO_4)_3:Tb^{3+}$, and $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$, as well as the standard pattern of $Ba_3La(PO_4)_3$ from Joint Committee on Powder Diffraction Standards (JCPDS) card. All XRD patterns were found to be in good agreement with JCPDS 29-0175 [$Ba_3La(PO_4)_3$], indicating that the obtained samples are single-phase and the doped Ce^{3+} and/or Tb^{3+} do not generate any impurity or induce significant changes in the host structure. In addition, no obvious shift of diffraction peaks can be observed, which is due to the similar ionic radius and the same valence state for Ce^{3+}/Tb^{3+} and La^{3+} ions.

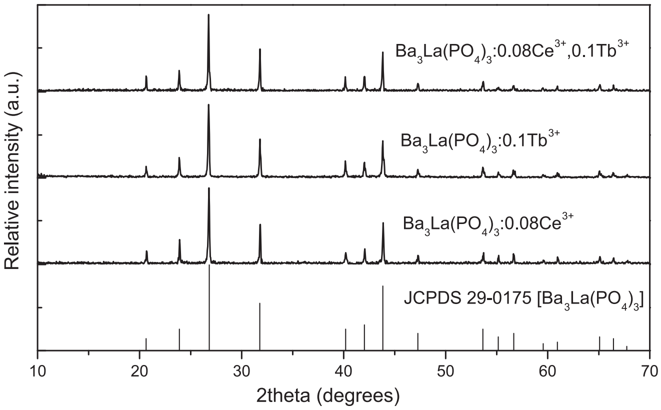

Fig. 1. Powder XRD patterns of $Ba_3La(PO_4)_3:Ce^{3+}$, $Ba_3La(PO_4)_3:Tb^{3+}$, and $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$, as well as the standard pattern of $Ba_3La(PO_4)_3$.

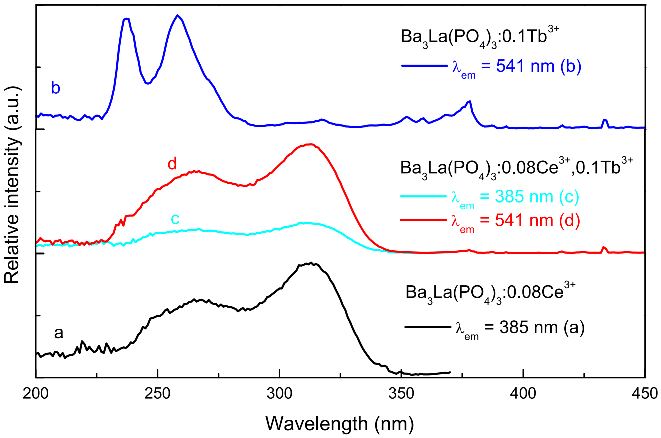

Fig. 2. Excitation spectra of $Ba_3La(PO_4)_3:Ce^{3+}$ (a), $Ba_3La(PO_4)_3:Tb^{3+}$ (b), and $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$ (c, d) by monitoring Ce^{3+} emission (385 nm) and/or Tb^{3+} emission (541 nm).

Fig. 2 shows the excitation spectra of $Ba_3La(PO_4)_3:Ce^{3+}$, $Ba_3La(PO_4)_3:Tb^{3+}$, and $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$ by monitoring Ce^{3+} emission (385 nm) and/or Tb^{3+} emission (541 nm). In curve a, the excitation spectrum of Ce^{3+} shows two broad bands centered at 267 nm and 312 nm, which are assigned to the 4f–5d transition of Ce^{3+} ions. In curve b, the excitation spectrum of Tb^{3+} presents broad 4f–5d excitation band (230–280 nm) and several 4–4f excitation lines (300–400 nm). In the excitation spectra of $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$, curves c and d are similar with curve a in shape, in which the excitation bands of Ce^{3+} ion are observed. As the monitoring emissions are different, so the observation of Ce^{3+} excitation band in excitation spectrum by monitoring Tb^{3+} emission in curve d gives crucial proof for the existence of ET from Ce^{3+} to Tb^{3+} in $Ba_3La(PO_4)_3$ host.

Fig. 3(a) shows the emission spectra of $Ba_3La_{0.92-x}Tb_xCe_{0.08}(PO_4)_3$ phosphors upon excitation with 312 nm. For $Ba_3La(PO_4)_3:Ce^{3+}$ (x=0), the emission spectrum shows a broad emission band peaking at 385 nm from UV – blue region, which is due to the 5D-4f transition of Ce^{3+} ions. When Tb^{3+} is co-doped in $Ba_3La(PO_4)_3:Ce^{3+}$, the typical ${}^5D_4 \rightarrow {}^7F_J$ ($J=6, 5, 4, 3$) emission lines of Tb^{3+} green emissions ranging from 470 to 700 nm are also observed. With the increase of Tb^{3+} concentration, two phenomenon can be observed. (1) The emission intensity of Ce^{3+} decrease gradually, indicating the $Ce^{3+} \rightarrow Tb^{3+}$ ET process is efficient; (2) The concentration quenching of ${}^5D_4$ emission intensity for Tb^{3+} ion was not evidently observed, which is similar with that the reported results for $Ba_3La_{1-x}Tb_x(PO_4)_3$ phosphors [15]. So the Tb^{3+}/Ce^{3+} emission ratio shows increasing tendency, which must lead to the change of luminous color for $Ba_3La(PO_4)_3:Ce^{3+},Tb^{3+}$ phosphors. The Commission International del'Eclairage (CIE) chromaticity coordinates of $Ba_3La_{0.92-x}Tb_xCe_{0.08}(PO_4)_3$ phosphors upon excitation with 312 nm were calculated and shown in Fig. 3(b), in which the CIE chromaticity coordinates shift systematically from blue (0.168, 0.089) for x=0 to yellowish-green (0.327, 0.528) for x=0.3 due to the increase of the Tb^{3+} concentration.

The decay curves of $Ba_3La_{0.92-x}Tb_xCe_{0.08}(PO_4)_3$ phosphors ($\lambda_{ex}=251.6$ nm, $\lambda_{em}=385$ nm) were monitored and shown in Fig. 3. All decay curves exhibit non-exponential decay behavior. So, the average lifetime (τ) was determined by the following formula [7,8,11]:

$$\tau = \frac{\int_{t0}^{\infty} tI(t)dt}{\int_{t0}^{\infty} I(t)dt} \tag{1}$$

where I(t) are the luminescence intensities at time t; t is the time; t0 is the initial time at which the luminescence intensities begin to decrease; τ is the average lifetime, respectively. As shown in Fig. 4, with the increase of Tb^{3+} concentration (x value), the average lifetime (τ) of Ce^{3+} show a decreasing tendency from 16.4 ns for x=0–4.3 ns for x=0.3, which testify the ET process from Ce^{3+} to Tb^{3+} in $Ba_3La_{0.92-x}Tb_xCe_{0.08}(PO_4)_3$ phosphors exists assuredly. Simultaneously, the ET efficiency (η) from Ce^{3+} to Tb^{3+} can also be expressed by the following equation [16],

$$\eta = 1 - \frac{\tau}{\tau_0} \tag{2}$$

in which τ and τ_0 are the lifetimes of Ce^{3+} with and without Tb^{3+} co-doping. The values of η were calculated to be 3.7%, 22.6%, 37.2%, 51.3%, 64.0% and 70.7% for $Ba_3La_{0.92-x}Tb_xCe_{0.08}(PO_4)_3$ phosphors with x=0.01, 0.03, 0.05, 0.1, 0.20, and 0.3, respectively. The above results indicate that the ET efficiency increases with the increasing of Tb^{3+} concentration in $Ba_3La_{0.92-x}Tb_xCe_{0.08}(PO_4)_3$ phosphors.

Generally, the exchange interaction and multipolar interaction are two main aspects responsible for the ET mechanism from a sensitizer to an activator in a phosphor [1,7]. When the critical distance (R) between the sensitizer and activator is less than 4 Å, the exchange interaction takes effect on the ET process; contrarily,