High luminescent brightness and thermal stability of red emitting $Li_3Ba_2Y_3(WO_4)_8$:Eu^{3+} phosphor

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A B S T R A C T

A series of $Li_3Ba_2Y_{3-x}(WO_4)_8$:xEu^{3+} ($x=0.1$, 1, 1.5, 2 and 2.8) phosphors were synthesized by a high temperature solid-state reaction method. Under the excitation of near ultraviolet (NUV) light, the as-prepared phosphor exhibits intense red luminescence originating from the characteristic transitions of Eu^{3+} ions, which is 1.8 times as strong as the commercial Y_2O_2S:Eu^{3+} phosphor. The optimal doping concentration of Eu^{3+} ions here is confirmed as $x=1.5$. The electric dipole-quadrupole (D-Q) interaction is deduced to be responsible for concentration quenching of Eu^{3+} ions in the $Li_3Ba_2Y_3(WO_4)_8$ phosphor. The analysis of optical transition and Huang-Rhys factor reveals a weak electron-phonon coupling interaction. The temperature-dependent emission spectra also indicate that the as-prepared $Li_3Ba_2Y_3(WO_4)_8$:Eu^{3+} phosphor has better thermal stability than that of the commercial Y_2O_2S:Eu^{3+} phosphor. Therefore, our results show that the as-prepared $Li_3Ba_2Y_3(WO_4)_8$:Eu^{3+} phosphor is a promising candidate as red emitting component for white light emitting diodes (LEDs).

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1. Introduction

As a replacement of traditional incandescent and fluorescent lamps, white light emitting diodes (WLEDs) have received people's great attention due to their excellent properties such as long life time, low energy consumption, environmental friendliness, high brightness and reliability [1–3]. Currently, the commercially available WLEDs are fabricated by combining a blue emitting chip (450–470 nm) with yellow emitting phosphor (YAG:Ce^{3+}) to achieve white light. However, the color rendering index (CRI) of this kind of white light is low due to their deficient emission in red spectral region [4]. An alternating approach to obtain white light via combining near ultraviolet (NUV) chips with tricolor (red, green and blue) phosphors is considering to be promising [5,6]. Unfortunately, the luminescence efficiency and thermal stability of red-emitting phosphor excited by NUV or blue light are still unsatisfied [2]. Thus, it is urgent to develop a efficient and stable red phosphor to meet the requirements for WLEDs.

For these reasons, recently tungstate phosphors have drawn much attention for their easy-synthesis, high luminescence efficiency and excellent thermal stability [7–9]. As one member of

tungstate family, the $Li_3Ba_2Y_3(WO_4)_8$ compound was first reported in 2009, which has a monoclinic system with space-group symmetry of $C2/c$, $a=5.181$ (Å), $b=12.677$ (Å), $c=19.161$ (Å), and $\beta=92.237°$ [10]. Due to the similar crystal structure, the distribution of Y^{3+}, Ba^{2+} and Li^{3+} ions over the M(1) and M(2) positions leads to the chemical formula $Li_2M(1)_2M(2)_4(WO_4)_8$, where M(1)= $Ba_{0.85}Y_{0.15}$, M(2)=$Y_{0.675}Ba_{0.075}Li_{0.25}$, and 90% of Y^{3+} ions occupy the M(2) sites, in the crystal of the $Li_3Ba_2Y_3(WO_4)_8$ according to Chang's paper [11]. The M(1) and M(2) sites are coordinated by five and eight oxygen atoms, respectively, and both sites lack inversion center symmetry [11]. Therefore, $Li_3Ba_2Y_3(WO_4)_8$ compound could be a suitable host for a Eu^{3+} doped phosphor with high color purity and brightness by induced $^5D_0 \rightarrow {}^7F_2$ red emission. However, up to now, there is no report on the red phosphors based on $Li_3Ba_2Y_3(WO_4)_8$ host by doping Eu^{3+} ions.

In this paper, we synthesized red emitting $Li_3Ba_2Y_3(WO_4)_8$: Eu^{3+} phosphors by solid-state reaction method, and their properties of the energy transfer, photoluminescence as well as temperature-dependent luminescence were investigated systematically. These samples present an intense red emission with chromaticity coordinates (0.659, 0.340) under the NUV excitation. Meanwhile, the detailed energy transfer mechanism of Eu^{3+} in $Li_3Ba_2Y_3(WO_4)_8$:Eu^{3+} system has been clarified. In addition, the temperature-dependent luminescence of the selected sample has been measured, which suggests its good thermal stability. These above results show that $Li_3Ba_2Y_3(WO_4)_8$:Eu^{3+} phosphors may have potential application for NUV pumped WLEDs.

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2. Experimental section

2.1. Preparation

A series of $Li_3Ba_2Y_{3-x}(WO_4)_8$:xEu^{3+} ($x=0.1$, 1, 1.5, 2 and 2.8) phosphors were synthesized via solid state reaction method. The raw materials including $LiCO_3$ (99.5%), $BaCO_3$ (99%), Y_2O_3 (99.99%), WO_3 (99.8%) and Eu_2O_3 (99.99%) were weighed according to the given stoichiometric ratios and ground thoroughly in an agate mortar for 1 h. Then the mixture was calcined in muffle furnace at 900 °C for 12 h. The final samples were ground again for further measurements when the furnace cooled to room temperature.

2.2. Characterization

The crystal structures of the as-prepared phosphors were checked on a Shimadzu XRD-6000 diffractometer equipped with Cu Kα_1 ($\lambda=0.15406$ nm) as the radiation source operating at 40 kV and 30 mA. The XRD data were gathered in the range of $10° \leq 2\theta \leq 70°$ with the step of 0.02°. Photoluminescence excitation (PLE) and emission (PL) spectra were measured on an Edinburgh FLS980 equipped with a 450 W xenon lamp as its excitation source. The decay curves were collected on an Edinburgh FLS980 equipped with a 100 W μF2 pulsed xenon lamp with pumping wavelength of 395 nm as the excitation resource. The temperature dependent photoluminescence spectra were obtained by using a homemade temperature control system in the range from 303 K to 573 K. The accuracy of the system was ± 0.5 °C.

3. Results and discussion

3.1. Structure analysis

The powder XRD patterns of the $Li_3Ba_2Y_{3-x}(WO_4)_8$:xEu^{3+} ($x=0.1$, 1, 1.5, 2 and 2.8) samples were displayed in Fig. 1, as well as the standard diffraction data of $Li_3Ba_2Y_3(WO_4)_8$ reported in crystallography open database (COD). It can be found that all the diffraction peaks are well consistent with the standard diffraction data (ID-7211787). No other diffraction peaks from impurities can be detectable, indicating that the as-prepared samples are single-phase and the introduction of Eu^{3+} ions does not significantly influence the crystal structure of the product.

3.2. Photoluminescence properties

The PLE and PL spectra of the representative phosphor $Li_3Ba_2Y_{1.5}Eu_{1.5}(WO_4)_8$ were presented in Fig. 2. In the PLE spectrum, a broad band from 230 to 300 nm and a series of narrow peaks from 300 to 500 nm can be observed when monitoring 615 nm emission. The broad band is ascribed to the charge transfer including $Eu^{3+} \rightarrow O^{2-}$ and $W^{6+} \rightarrow O^{2-}$, but the contribution of the two components cannot be distinguished easily due to spectral overlap. The narrow peaks correspond to the characteristic f-f transitions of Eu^{3+}, in which the two intense peak centered at 395 and 465 nm is ascribed to $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ transition, indicating the $Li_3Ba_2Y_3(WO_4)_8$:Eu^{3+} phosphor can be excited efficiently by NUV (250–400 nm) and blue LED chips (430–470 nm). The other peaks are ascribed to $^7F_0 \rightarrow {}^5H_6$, $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_3$, $^5L_7$ and $^7F_0 \rightarrow {}^5D_3$ transitions of Eu^{3+} ion, respectively. Under the excitation of 395 nm, the emission spectrum of $Li_3Ba_2Y_3(WO_4)_8$:Eu^{3+} exhibits four peaks centered at 585, 615, 655 and 703 nm due to the $^5D_0 \rightarrow {}^7F_J$ ($J=1$, 2, 3 and 4) transitions of Eu^{3+}, respectively. It is known that the $^5D_0 \rightarrow {}^7F_J$ emission of the Eu^{3+} ion has a close relationship with its occupied chemical environment. When the Eu^{3+} ion was located at site with inversion symmetry, the
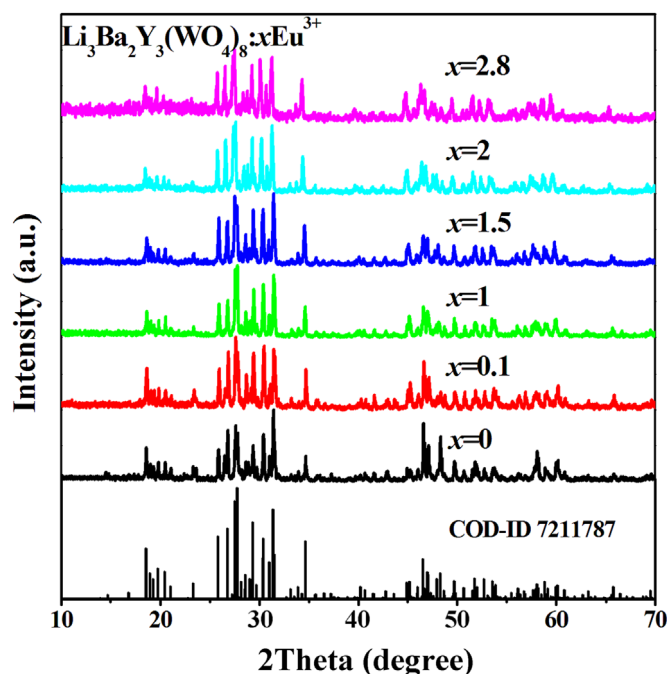

Fig. 1. The XRD patterns of $Li_3Ba_2Y_{3-x}Eu_x^{3+}$ $(WO_4)_8$ ($x=0.1$, 1, 1.5, 2 and 2.8) phosphors.
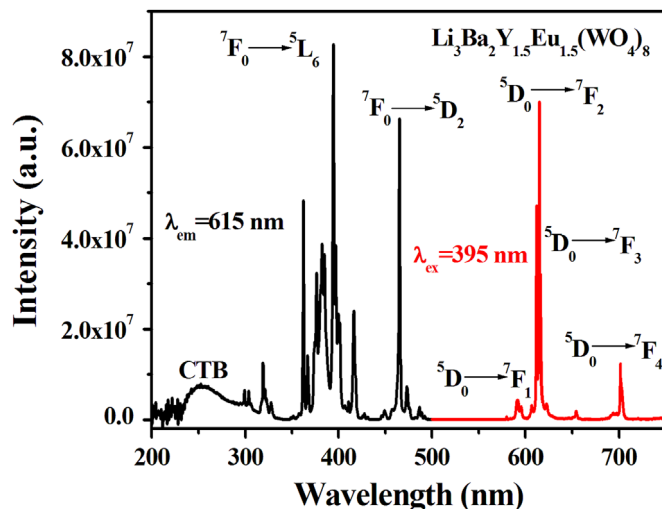
Fig. 2. Excitation and emission spectra of $Li_3Ba_2Y_{1.5}Eu_{1.5}(WO_4)_8$ phosphor.

magnetic dipole ($^5D_0 \rightarrow {}^7F_1$) transition was dominant, whereas at site without inversion symmetry, the electric dipole ($^5D_0 \rightarrow {}^7F_2$) transition was dominant [12]. In this work, as can be seen in emission spectrum in Fig. 2, the electric dipole transition $^5D_0 \rightarrow {}^7F_2$ centered at 615 nm dominates the whole emission spectra obviously, which suggests Eu^{3+} ions are located at the asymmetric inversion center.

In order to explore the luminescent performance of as-prepared samples, the effect of the doping concentration of Eu^{3+} ions on the emission intensity of the $Li_3Ba_2Y_{3-x}(WO_4)_8$:xEu^{3+} phosphors ($x=0.1$, 1, 1.5, 2 and 2.8) were studied and the emission spectra upon 395 nm excitation were displayed in Fig. 3. As can be seen, the profiles of emission spectra are similar to each other, which can confirm that there is only one Eu^{3+} emission center at Y^{3+} sites. And as mentioned above, every spectrum consists of four sharp lines ranging from 580 to 750 nm, which are attributed to the $^5D_0 \rightarrow {}^7F_J$ ($J=1$, 2, 3 and 4) transitions. Here, on the basis of