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Energy transfer and tunable photoluminescence of $LaBWO_6:Tb^{3+},Eu^{3+}$ phosphors for near-UV white LEDs

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ABSTRACT

Tb^{3+} and Eu^{3+} ion co-doped $LaBWO_6$ phosphors with tunable color emissions were synthesized by a conventional high-temperature solid-state reaction technique and were characterized by powder X-ray diffraction, scanning electron microscope, emission and excitation spectra, and decay lifetimes. Under 380 nm near-ultraviolet excitation, the characteristic visible emissions, which originate from the f–f transitions of Tb^{3+} and Eu^{3+} ions, were observed in the emission spectra. By increasing of the Eu^{3+}/Tb^{3+} concentration ratio, the $LaBWO_6:Tb^{3+},Eu^{3+}$ phosphors were capable of generating color tunability from green to yellow, then to red. The energy transfer process between Tb^{3+} and Eu^{3+} was demonstrated to be a resonant type via a dipole–dipole mechanism, and the critical distance calculated by the concentration quenching method was determined to be 11.1 Å. Moreover, the temperature-dependent emission spectra showed that the as-prepared phosphors possessed good thermal stability with an activation energy of 0.263 eV. These $LaBWO_6:Tb^{3+},Eu^{3+}$ phosphors with tunable emissions may have potential applications in near-ultraviolet-pumped white light-emitting diodes.

1. Introduction

During the past decades, inorganic luminescent materials based on rare-earth ions have been widely studied because of their important applications in diverse fields, including lightings, displays, solar cells, lasers, sensors, and bioimaging [1–21]. The white light-emitting diodes (LEDs) have been regarded as a new generation of light source, due to their unique advantages such as long lifetimes, energy saving, mercury free and high reliability. At present, the commercial white LEDs are generally fabricated by combining the blue LED chips with $Y_3Al_5O_{12}:Ce^{3+}$ yellow-emitting phosphors. However, the lack of a red component leads to low color rendering index (CRI $<$ 80) and a high correlated color temperature (T_c $>$ 4500 K), which limits their applications in indoor lighting. To solve these problems, an alternative approach that uses the ultraviolet (UV) LED chip to pump the tricolor (red, green and blue) phosphors was recently proposed. By adjusting the ratios of tricolor phosphors, the white light can be easily achieved. However, LED devices based on mixing multiple phosphors have an inevitable drawback of fluorescence re-absorption between different components and non-uniformity of the luminescence properties, which finally leads to the decrease of luminous efficiency and the deviation from color point over time for white LEDs. Thus, it is of great importance to develop single-phased phosphors with tunable multicolor emission under a single excitation wavelength for near-UV white LEDs.

Co-doping multiple activator ions into a single-phased host material based on ET mechanism has been regarded to be an effective strategy to achieve tunable multicolor emission [22–28]. Tb^{3+} and Eu^{3+} ions have been widely used as activators in phosphors for lighting and display applications [29–33], due to their efficient green and red emissions, respectively. Moreover, Tb^{3+} ion has been proven to be a good sensitizer for Eu^{3+} ion, and tunable luminescence were observed in Tb^{3+} and Eu^{3+} co-doped phosphors via changing the concentration ratio of Tb^{3+}/Eu^{3+}. Consequently, Tb^{3+} and Eu^{3+} ion co-doped multicolor emitting phosphors could be used in near-UV-pumped white LED devices. Significantly, choosing a suitable host is very important for developing efficient phosphors. As is known to all, the simple and double crystals are widely explored in laser and photonic technologies because of their specific structural, thermal and electronic characteristics, high chemical stability and excellent spectroscopic properties [34–37]. As a novel member of the scheelite structure tungsten borate, $LaBWO_6$ phosphor belongs to the orthorhombic structure, associated with the space group of P_{222}, and lattice parameters of a = 0.410, b = 1.031,

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c = 2.171 nm [38]. The vacuum ultraviolet and cathodoluminescence were studied for $LaBWO_6$ [39–42], but, there is no report on energy transfer (ET) between Tb^{3+} and Eu^{3+} ions and unknown the potential for white LEDs application.

In this paper, we reported on the tunable multicolor luminescence in Tb^{3+} and Eu^{3+} co-doped $LaBWO_6$ phosphors prepared by a conventional high-temperature solid-state reaction technique. Under 380 nm near-UV excitation, $LaBWO_6:Tb^{3+},Eu^{3+}$ phosphors showed intense visible emissions as a result of ET from Tb^{3+} to Eu^{3+}, and emission color is continuously tuned from green to red by adjustment of Eu^{3+}/Tb^{3+} content ratio. The ET from Tb^{3+} to Eu^{3+} was systematically investigated by the luminescence spectra, ET efficiency, and lifetime measurements. These results indicated that the $LaBWO_6:Tb^{3+},Eu^{3+}$ multicolor emitting phosphors have potential applications for near-UV-pumped LEDs.

2. Experimental

The $La_{0.99\text{-}x}BWO_6:0.01Tb^{3+},xEu^{3+}$ (x = 0.005, 0.01, 0.02, 0.05, 0.1, and 0.2) phosphors were successfully prepared via a conventional high-temperature solid-state reaction technique. H_3BO_3 (analytical reagent), $(NH_4)_{10}H_2(W_2O_7)_6$ (analytical reagent), La_2O_3 (99.99%), $Tb(NO_3)_3{\cdot}6H_2O$ (99.99%), and Eu_2O_3 (99.99%) were used as the raw materials. According to the stoichiometric ratio, these raw materials were weighted and ground in an agate mortar to achieve uniformity. In order to compensate the volatilization, the amount of H_3BO_3 is in excess of 10 wt%. Then, these uniform mixtures were put in the alumina crucibles and sintered at 1000 °C for 4 h. After finishing the reaction, the furnace cooled down naturally to room temperature, and the final products were ground and collected for further characterization.

The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 X-ray diffractometer using Cu Kα radiation ranging with 10–55° at step rate of 0.02°. The morphology properties of the samples were obtained by a field-emission scanning electron microscope (FE-SEM; MAIA3 TESCAN). The room-temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra and luminescence decay lifetimes of phosphors were measured by Edinburgh FS5 spectrometer equipped with a 150 W continued-wavelength Xenon lamp and a pulsed Xenon lamp, respectively.

3. Results and discussion

3.1. Phase and structure

Fig. 1 shows the XRD patterns of $La_{0.99}BWO_6:0.01Tb^{3+}$ and $La_{0.985}BWO_6:0.01Tb^{3+},0.005Eu^{3+}$ phosphors. All the obtained patterns agreed well with the Joint Committee on Powder Diffraction Standards (JCPDS) of Card No. 35-0261, which are consistent with the pure crystalline orthorhombic $LaBWO_6$ with a space group of P_{222}. No diffraction peak corresponding to any impurity or allotropic phase was observed, indicating that a pure crystalline compound was obtained.

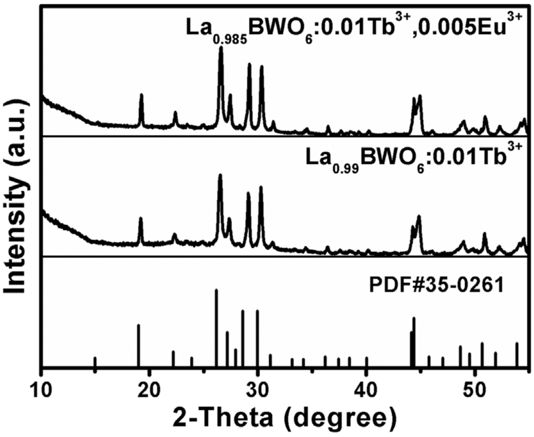

Fig. 1. XRD patterns of $La_{0.99}BWO_6:0.01Tb^{3+}$ and $La_{0.985}BWO_6:0.01Tb^{3+},0.005Eu^{3+}$ phosphors. The standard data of $LaBWO_6$ (JCPDS 35-0261) was shown.

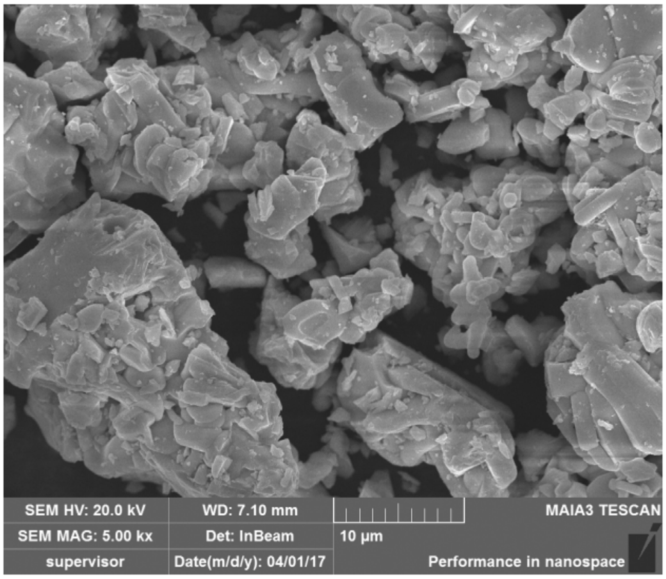

Fig. 2. FE-SEM images of $LaBWO_6:0.01Tb^{3+},0.005Eu^{3+}$ phosphors.

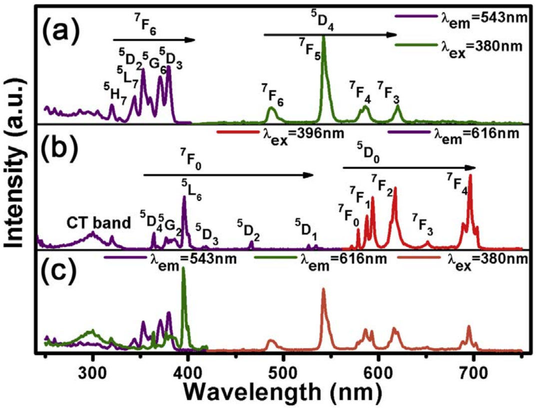

Fig. 3. Excitation and emission spectra of (a) $La_{0.99}BWO_6:0.01Tb^{3+}$, (b) $La_{0.99}BWO_6:0.01Eu^{3+}$, and (c) $La_{0.985}BWO_6:0.01Tb^{3+},0.005Eu^{3+}$ phosphors.

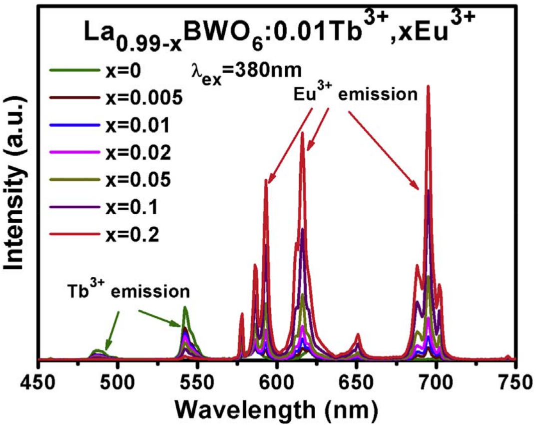

Fig. 4. Emission spectra of $La_{0.99\text{-}x}BWO_6:0.01Tb^{3+},xEu^{3+}$ (x = 0.005, 0.01, 0.02, 0.05, 0.1, and 0.2) phosphors excited at 380 nm.