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Original research article

Synthesis and enhanced luminescence properties of BaB_2O_4: Eu^{3+} microphosphor prepared from the $Ba_3B_6O_9(OH)_6$:Eu^{3+} precursor

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ABSTRACT

The novel $Ba_3B_6O_9(OH)_6$:Eu^{3+} with brick-like microstructure were prepared using the hydrothermal method. BaB_2O_4:Eu^{3+}(BBO-A) with sheet-like microstructure were obtained firstly by calcining $Ba_3B_6O_9(OH)_6$:Eu^{3+}. For comparison, the BaB_2O_4:Eu^{3+} (BBO-B) with block-like morphology was prepared by the conventional solid-state method. The possible reaction and growth mechanisms of $Ba_3B_6O_9(OH)_6$:Eu^{3+} and BaB_2O_4:Eu^{3+} were proposed. The structure, morphology and luminescent properties of BaB_2O_4:Eu^{3+} and $Ba_3B_6O_9(OH)_6$:Eu^{3+} were studied. It was found that BaB_2O_4:Eu^{3+} shows much stronger emission intensity than $Ba_3B_6O_9(OH)_6$:Eu^{3+},and the emission peak position of BaB_2O_4:Eu^{3+} is red-shifted compared with the $Ba_3B_6O_9(OH)_6$:Eu^{3+}. In addition, the results showed that BBO-A exhibit stronger emission intensity and better red color purity than BBO-B, this indicates that the luminescent properties of BaB_2O_4:Eu^{3+} phosphor was enhanced by the two-step hydrothermal approach through further calcination process.

1. Introduction

White light-emitting diodes (WLEDs) have attracted an increasing interest because of their widely application and their superior properties [1,2].There is an urgent need to find the phosphor with high luminescent efficiency for use in UV-excited WLED as the classical phosphors are not good enough for its application. Borate has become an excellent host for red-emitting phosphors due to its high stability, high luminescent efficiency and low synthetic temperature, etc. To date, some of red-emitting borate phosphors which can be used for WLEDs have been prepared and studied [3–7]. BaB_2O_4 was chosen as the host for phosphors due to its high transparency and exceptional optical damage threshold [8,9], various techniques have been developed for its typically including high temperature solid state methods [10,11], co-precipitation [12–14] and hydrothermal method [15]. It was reported that some other phosphors prepared by two-step hydrothermal method, the hydrothermal method prepared precursor is further heated, exhibit higher purity, stronger luminous intensity and better morphology than the phosphors which were prepared by conventional solid-state method [16,17], however, this has not been confirmed for BaB_2O_4 phosphor, and controlling the structure and morphology of products by this method is still difficult. It was reported that the structure, morphology, properties of precursor have great impact on that of products [18–21]. It is the necessary, therefore, to study the relationship between the precursor and the products. To our knowledge, only one paper reported the synthesis of BaB_2O_4 based phosphors by two-step hydrothermal method [15], however, there is no study on the relationship between the precursors and the products.

In this work, the BaB_2O_4:Eu^{3+} phosphors were obtained by a two-step hydrothermal method using $Ba_3B_6O_9(OH)_6$:Eu^{3+} as the precursor, the influence of structure, morphology and luminescence behaviors of the precursor on that of BaB_2O_4:Eu^{3+} were studied,

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and the reaction and growth mechanisms were discussed. The comparative study of the two-step hydrothermal method and the conventional solid state reaction method has also been carried out.

2. Experimental

2.1. Synthesis of samples

2.1.1. Synthesis of precursors

The $Ba_3B_6O_9(OH)_6$:Eu^{3+} named BBOH was synthesized using hydrothermal method. 4 mmol of $Ba(NO_3)_2$ and 5 mol% of $Eu(NO_3)_3$ were firstly dissolved in 40 mL H_2O, then 40 mL 0.15 mol/L of $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ solution was added. After stirring for 30 min, the resulting slurry was poured into autoclave, and heated at 240 °C for 24 h. Finally, the precipitate was washed with ethanol and distilled water, followed by drying at 40 °C for 24 h.

2.1.2. Synthesis of BaB_2O_4:Eu^{3+}

The BaB_2O_4:Eu^{3+} named BBO-A was synthesized by calcining the $Ba_3B_6O_9(OH)_6$:Eu^{3+} at 800 °C for 5 h in air. The BaB_2O_4:Eu^{3+} named BBO-B was obtained by conventional solid-state method at 800 °C for 5 h using Eu_2O_3, $BaCO_3$ and H_3BO_3 (3% excess) as raw materials.

2.2. Characterization

The composition of the products are characterized by Rigaku D/MAX-C X-ray powder diffraction with CuKα radiation (λ = 1.540 Å) and Hitachi, JEOL-6700 F energy dispersive X-ray spectrometer. Fourier transform infrared spectroscopy analysis was carried out by using a Bruker EQUINOX55 spectrophotometer at room temperature. The morphologies of the samples were observed via Philips-FEI, Quanta200 scanning electron microscopy. The photoluminescence (excitation and emission) spectra of samples were detected by Hitachi, FL-4600 spectrophotometer.

3. Results and discussions

3.1. Phase identification and morphology

The XRD patterns of the $Ba_3B_6O_9(OH)_6$:Eu^{3+} is shown in Fig. 1(a). It can be seen that the $Ba_3B_6O_9(OH)_6$:Eu^{3+} is well crystallized and all the diffraction peaks agreed with JCPDS file No. 01-071-2501 of the $Ba_3B_6O_9(OH)_6$ and the previous report [22,23]. No characteristic peaks of impurities, other borates and un-reacted compounds were observed in these samples indicating that Eu^{3+} ions were completely doped in the $Ba_3B_6O_9(OH)_6$ lattice. The XRD patterns of the BaB_2O_4:Eu^{3+} is shown in Fig. 1(b,c). The diffraction peak position of two samples are almost the same except the peak intensity and it is well matched with that of BaB_2O_4 (JCPDS No.24-0086). It indicates the BaB_2O_4:Eu^{3+} can be prepared successfully by calcinning $Ba_3B_6O_9(OH)_6$:Eu^{3+} precursors. The BBO-A exhibit stronger peak intensity than BBO-B meaning that it has higher crystallinity.

Fig. 2 shows the FT-IR spectra of the $Ba_3B_6O_9(OH)_6$:Eu^{3+} and BaB_2O_4:Eu^{3+}. In Fig. 2(a), the bands at 3464 cm^{-1} are the stretching of O—H. The peak at 1198 cm^{-1} is the in-plane bending of B—O—H. The peaks at 835,544 cm^{-1} are attributed to the vibration of tetraborate $(BO_4)^{5-}$ groups [24], which are the basic units of the $Ba_3B_6O_9(OH)_6$ structure [22]. The FT-IR spectrum of the BaB_2O_4:Eu^{3+} is shown in Fig. 2(b,c). The infrared spectrum of the two samples are similar, the peak at 1636 cm^{-1} is the H—O—H bending vibration of the H_2O molecule, the existence of water may arise from moisture absorbed during the measurement. The peaks

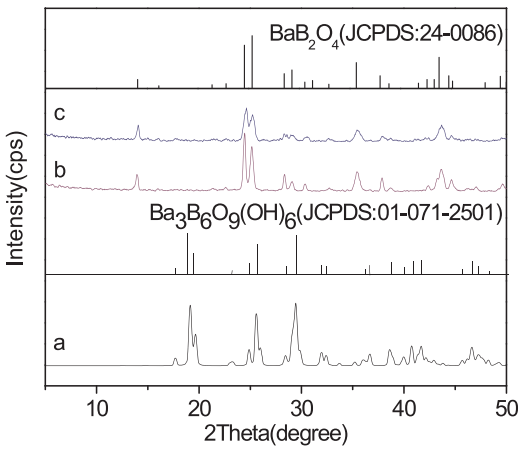

Fig. 1. XRD patterns of $Ba_3B_6O_9(OH)_6$:$0.05Eu^{3+}$ and BaB_2O_4:$0.05Eu^{3+}$: (a) BBOH, (b) BBO-A, (c) BBO-B.