



Luminescence properties in relation to controllable morphologies of the $\text{InBO}_3:\text{Eu}^{3+}$ phosphor



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ABSTRACT

Four kinds of morphologies of Eu^{3+} doped indium borate of the InBO_3 phosphors have been prepared via a facile flux method only by adjusting the kinds of reaction boron source materials, which have been characterized by XRD, EDS and SEM. In addition, the doping concentration also has a great influence on the morphology of samples. Furthermore, the luminescence properties of the prepared $\text{InBO}_3:\text{Eu}^{3+}$ samples have been investigated by photoluminescence (PL) spectra. The results show that the fluorescence performance is strongly correlated with morphologies. The prepared $\text{InBO}_3:\text{Eu}^{3+}$ phosphors show strong orange emissions under ultraviolet excitation at 237 nm, in which the monodisperse octahedra sample prepared with $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ as the boron source and Eu^{3+} doping concentration being 5% possesses the higher PL intensity and color purity, which can be used as a potential orange luminescent material.

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1. Introduction

In recent years, rare-earth (RE) doped materials have been proposed for a variety of applications including solid state lasers, displays, low intensity IR imaging, watermarking technology, 3D storage media, solar cells, and biological probes [1]. Among various host materials, borate triggered increasing research interest not only owing to its rich structural chemistry but also because of its large band gap, high thermal stability, high luminescence efficiency and low cost [2]. Until now, some RE doped InBO_3 phosphors have been synthesized through a sol-gel technology [3–5] or a two-step solid state method [6] for different applications. Nevertheless, both methods need high temperature, leading to a poor morphology. The present used flux method has the advantage of simple operation, lower temperature and short reaction time [7].

The properties and applications of luminescent materials have a strong dependence on their chemical composition, crystal structure, size and morphology. Hence, controlling the size and shape of existing materials precisely enables us to manipulate their properties as desired [8,9]. To date, many

researchers have prepared different kinds of RE doped inorganic phosphors through changing different source materials, such as the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor with different morphology prepared by a high-temperature solid-state reaction method using different phases of Al_2O_3 [10], the $\beta\text{-Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor prepared by a novel liquid-phase-precursor method utilizing $\text{CaCl}_2/\text{Ca}(\text{NO}_3)_2\text{-EuCl}_3/\text{Eu}(\text{NO}_3)_3$ combinations [11], and Ln^{3+} ($\text{Ln}=\text{Tb}, \text{Eu}$) doped zinc phosphate with different morphology by altering the phosphate sources [12]. Recently, there are several new reports about preparation of rare-earth doped luminescent materials and tuning of luminescence properties by morphologies [13–18].

InBO_3 with high band gap of 5.6 eV has been proposed as a promising host material for optically active materials such as the rare earth ions [5]. As the host matrix in the phosphor, it exhibits high transparency in the ultraviolet (UV) and VUV region, good chemical stability, high refractory properties and high optical quality [5]. In this work, a variety of morphologies of $\text{InBO}_3:\text{Eu}^{3+}$ luminescent materials were first prepared via a facile flux method by using different boron sources. The relationship between morphologies and fluorescence properties was also investigated.

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2. Experimental

2.1. Preparation of samples

$\text{InBO}_3:\text{Eu}^{3+}$ phosphors were synthesized using a facile flux method with the raw materials (A.R. grade) of In_2O_3 , B_2O_3 / $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ / $\text{Li}_2\text{B}_4\text{O}_7$ / $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ and Eu_2O_3 according to a certain stoichiometric mole ratio of 0.97:15:0.03. The amounts of raw materials were weighted out, well-mixed and ground thoroughly in an agate mortar. Then the mixture was transferred into 10 mL teflon-lined autoclaves, adding 0.65 mL water, which was sealed and maintained at 220 °C for 72 h. After cooling to room temperature, the white products were obtained by filtering, washing with deionized water and ethanol for several times and drying at 60 °C for 12 h.

2.2. Measurement and characterization

All samples were characterized by power X-ray diffraction (XRD; recorded on a Rigaku D/max with Cu target at a scanning rate of 8°/min with 2θ range from 10° to 70°), energy dispersive X-ray spectrometry (EDS), and field emission scanning electron microscope (SEM; SU-8020, Hitachi High-Tech Company). The emission and excitation spectra were measured with a Hitachi F-7000 spectrophotometer equipped with a continuous 150W Xe-arc lamp at room temperature.

3. Results and discussion

3.1. The effect of different boron source materials on the morphologies of the samples

Fig. 1 shows the XRD and EDS patterns of 3% Eu^{3+} doped samples prepared with different boron sources. It is observed that all the XRD diffraction peaks are similar and can be perfectly indexed as InBO_3 (ICDD card No. 17-0933). There are no diffraction peaks of impurities detected. The doping of Eu^{3+} did not change the crystal structure of InBO_3 . The EDS patterns of the sample clearly indicate that the obtained sample contains B, O, In and Eu elements, and no other impurity element peaks can be found. From these results, we can conclude that the Eu^{3+} ions doped phosphors were prepared successfully.

Fig. 2 shows the SEM images of 3% Eu^{3+} doped samples prepared with different boron sources. It can be seen that the different boron source materials have significant effects on

morphologies of samples. When using B_2O_3 as the boron source, the sample exhibits smooth monodisperse microsphere morphology with diameter of about 3 μm (Fig. 2a). The similar morphology can be obtained when using H_3BO_3 as boron source. When using $\text{NH}_4\text{B}_5\text{O}_7 \cdot 4\text{H}_2\text{O}$ as boron source, the obtained sample exhibited monodisperse flat microsphere with a hole morphology with diameter of about 3 μm and thickness of about 1.5 μm (Fig. 2b). When using $\text{Li}_2\text{B}_4\text{O}_7$ as boron source, the sample exhibited rough monodisperse octahedron morphology with edge of about 5 μm (Fig. 2c). When using $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ as boron source, the sample exhibited smooth oblique hexahedron morphology with edge of about 3.5 μm (Fig. 2d). The similar morphology can be obtained when using $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ as boron source.

High resolution TEM images of obtained samples at different boron sources are shown in Fig. 3. In Fig. 3a, the interplanar distances of the crystal fringes of the sample obtained with B_2O_3 as boron sources are 0.26 nm and 0.35 nm, respectively, which are very close to the d values (0.26 nm and 0.37 nm) of the (0 0 6) and (0 1 2) facets. In Fig. 3b, the interplanar spacing of obtained sample with $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ as boron sources is 0.28 nm, which is very close to the d value (0.28 nm) of the (0 1 $\bar{4}$) facet. In Fig. 3c, the interplanar distance of the crystal fringes of obtained sample with $\text{Li}_2\text{B}_4\text{O}_7$ as boron sources are 0.30 nm and 0.22 nm, respectively, which are very close to the d values (0.28 nm and 0.22 nm) of the (0 1 $\bar{4}$) and (1 1 3) facets. In Fig. 3d, the interplanar distance of the crystal fringes of obtained sample with $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ as boron sources are 0.30 nm and 0.35 nm, respectively, which are very close to the d values (0.28 nm and 0.37 nm) of the (0 1 $\bar{4}$) and (0 1 2) facets. It can be seen that the obtained samples at different boron sources have the different growth directions, which lead to their different final morphologies.

The formation process of the different morphologies can be explained by a two-stage growth process. In the first stage, the reaction taken place through a fast nucleation step to form many amorphous primary particles. In the second stage, the primary particles crystallized, followed by aggregation and anisotropic growth to form diverse morphologies [12]. When the different boron source materials were introduced into the reaction system, the pH values and the existing cations could be different. The pH values of final solution were 5, 6, 7, and 9, when using B_2O_3 , $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$, $\text{Li}_2\text{B}_4\text{O}_7$ and $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ as boron sources, respectively. The pH value can affect the kinds and qualities of absorbed ions in the surface of crystal. Thus, the surface energy of crystal is different. According to the Gibbs-Curie-Wulff theorem, the growth rates on different surface facets are dominated by the

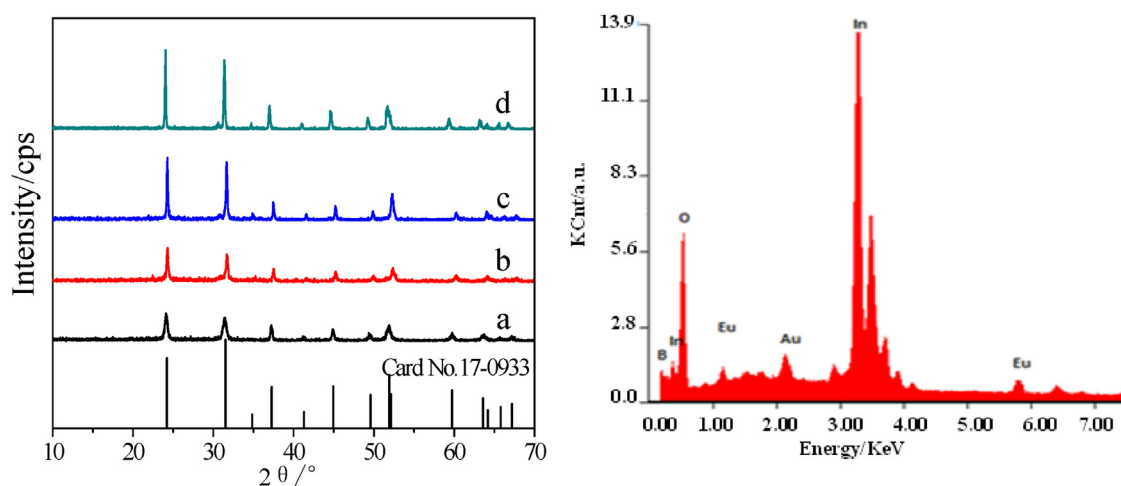


Fig. 1. XRD and EDS patterns of $\text{InBO}_3:\text{Eu}^{3+}$ samples obtained at different boron sources: (a) B_2O_3 , (b) $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$, (c) $\text{Li}_2\text{B}_4\text{O}_7$, (d) $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$.

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