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Synthesis and spectroscopic studies of $Zn_4B_6O_{13}$ and Eu/Tb single-doped $Zn_4B_6O_{13}$ phosphors

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Abstract: In this study, $Zn_4B_6O_{13}$, Eu- and Tb-doped $Zn_4B_6O_{13}$ phosphors were prepared by conventional solid state reaction method and the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectroscopy (PL). The doped rare-earth ions had little influence on the crystal structure of $Zn_4B_6O_{13}$, but obviously affected the morphology of $Zn_4B_6O_{13}$ particles. The PL results indicated that the 5% Eu-doped sample and 1% Tb-doped sample had the highest intensity in their respective different concentrations doped samples. The CIE chromaticity coordinates indicated that $Zn_4B_6O_{13}$, $Zn_4B_6O_{13}$:Eu and $Zn_4B_6O_{13}$:Tb showed the three basic colors of blue, red and green, respectively. Evidently, the white light could appear only at appropriate intensity of blue, red and green components.

Keywords: zinc borate; $Zn_4B_6O_{13}$; rare earth ions; phosphor

White light-emitting diodes (w-LEDs) have been regarded as the new generation of illumination source due to numerous advantages, such as long lifetime, energy saving properties, environmental friendliness, etc. However, the commonly used w-LEDs, which are based on the combination of a blue InGaN LED chip and a yellow emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce), have a low color rendering index and a high color temperature due to the lack of red-emitting component. At present, researchers overcome above problems by combining a near-UV LED chip with a white-emitting phosphor or the mixture of blue, green and red emitting phosphors. Therefore, it is important to search for phosphors that can be excited efficiently by near-UV LEDs[1–5]. As a red emitting phosphor, the Eu^{3+}-doped compounds are recognized as efficient red color components due to their $^5D_0\rightarrow{}^7F_J$ (J=0, 1, 2, 3, 4) transitions[6–9]. For a green emitting phosphor, Tb^{3+}-doped compounds are considered as attractive candidates because the $^5D_4\rightarrow{}^7F_5$ transition of Tb^{3+} is around 540 nm[10,11]. In principle, Tb^{3+} as a green activator has lower threshold pump power compared with Er^{3+} ions and shorter decay time than Mn^{2+} ion[12,13]. For a blue emitting phosphor, some kinds of borates can be recognized as an blue luminescent phosphors due to their self-trapped excitons (STE)[14].

Zinc borates are multifunction materials with different ratios of ZnO, B_2O_3 and H_2O. They are very important chemical raw materials which have been widely used in various fields. They are extensively used in polymer retardant flame material[15]. In recent years, zinc borate obtained more and more attention as a host material for luminescence applications. For instance, Qiao et al. prepared a series of Eu^{3+} doped $Zn[B_3O_3(OH)_5]\cdot H_2O/ZnB_4O_7/ZnB_2O_4$ phosphors by a facile method[16]. Erdoğmuş et al. synthesized Tb^{3+} doped $Bi_2ZnB_2O_7$ by conventional solid state reaction method[17]. Shanmugavelu et al. prepared Nd^{3+} doped bismuth zinc borate glasses by melt quenching method[18]. Ravi et al. prepared Dy^{3+} ions doped niobium containing tellurium calcium zinc borate (TCZNB) glasses by the melt quenching method[19].

In this study, the $Zn_4B_6O_{13}$, Eu- and Tb-doped $Zn_4B_6O_{13}$ phosphors were synthesised by the solid state reaction method and the photoluminescence properties were evaluated. The CIE chromaticity coordinates indicated that the phosphor possessed blue, red and green emitting, respectively.

1 Experimental

1.1 Synthesis of samples

All the investigated phosphors were synthesized with traditional solid state reactions. Firstly, raw materials $ZnCl_2$ (A.R., ≥98%), $NH_5B_5O_8\cdot 3H_2O$ (A.R., 98%), Eu_2O_3 (A.R., 99.9%), Tb_4O_7 (A.R., 99.9%) were accurately weighed according to the composition of $Zn_4B_6O_{13}$, $Zn_4B_6O_{13}:xLn^{3+}$ (x=0.1%, 0.5%, 1%, 3%, 5% and 7%; % refers to mol.% hereinafter; Ln=Eu and Tb). The weighed materials were thoroughly ground and, then, the

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mixture was transferred into a platinum crucible. The platinum crucible was placed into a muffle furnace and, then, heated at 900 ºC in air for 3 h. After being cooled to room temperature, the obtained samples were ground for structure characterization and luminescent study.

1.2 Characterization

The phase compositions of the samples were characterized by X-ray diffraction (XRD, RigakuD/MAX-C, Cu Kα radiation at 40 kV and 30 mA) analysis. The micromorphology and particle size for all samples were characterized by field scanning electron microscopy (FSEM) (SU-8020, Hitachi). The photoluminescence excitation (PLE) and emission (PL) spectra were recorded at room temperature on a molecular fluorescence spectrometer (FL-7000, Hitachi) equipped with a 150 W xenon lamp as the excitation source.

2 Results and discussion

2.1 Characterization of samples

The XRD patterns of undoped samples are shown in Fig. 1. It is observed that all the peaks in Fig. 1(a) are in good agreement with those of the cubic phase (space group: *I*-43*m*) $Zn_4B_6O_{13}$ (PDF#27-1487). There are no diffraction peaks of foreign crystalline phases or impurities detected in the XRD patterns, indicating that the as-prepared sample is single-phase state. In the $Zn_4B_6O_{13}$ structure, all boron atoms are four-coordinated by oxygen atoms. The tetrahedral borate groups BO_4 are linked to each other forming a three-dimensional framework[20]. The XRD patterns of Eu- and Tb-doped samples are listed in Fig. 1(b, c). All the peaks in Fig. 1(b, c) are in good agreement with those of the cubic phase (space group: *I*-43*m*) $Zn_4B_6O_{13}$ (PDF#27-1487). But there exist some weak peaks in the high doped concentration samples between 25º to 30º, which can be ascribed to $Zn_3(BO_3)_2$.

The FSEM images of pure and doped samples are shown in Fig. 2(a, b, c). It is apparent that the undoped $Zn_4B_6O_{13}$ displays the faceted polyhedron morphology with the edge ~20 µm in size (Fig. 2(a)). The FSEM pattern of $Zn_4B_6O_{13}$:5%Eu displays the irregular morphology with the average particle size about 10 µm (Fig. 2(b)). The $Zn_4B_6O_{13}$:5%Tb particles are also irregular in morphology and they possess the characteristic size

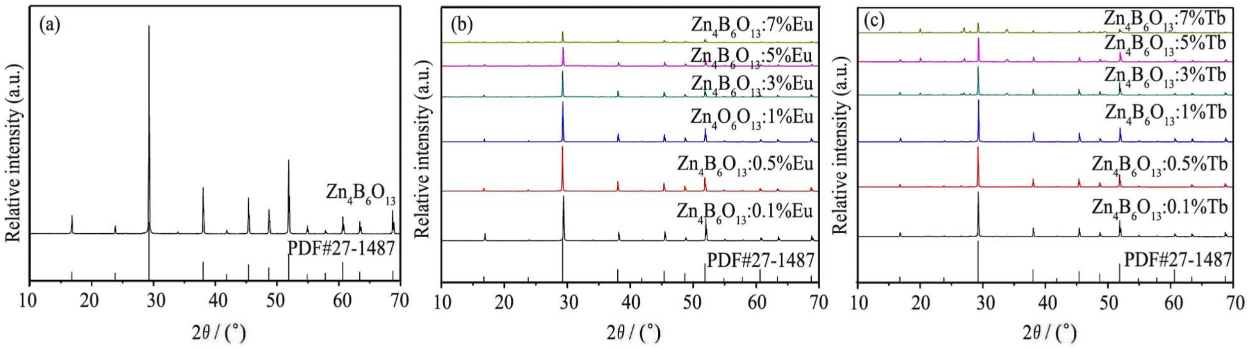

Fig. 1 XRD patterns of $Zn_4B_6O_{13}$ (a), $Zn_4B_6O_{13}$:*x*%Eu (*x*=0.1, 0.5, 1, 3, 5, 7) (b) and $Zn_4B_6O_{13}$:*x*%Tb (*x*=0.1, 0.5, 1, 3, 5, 7) (c)

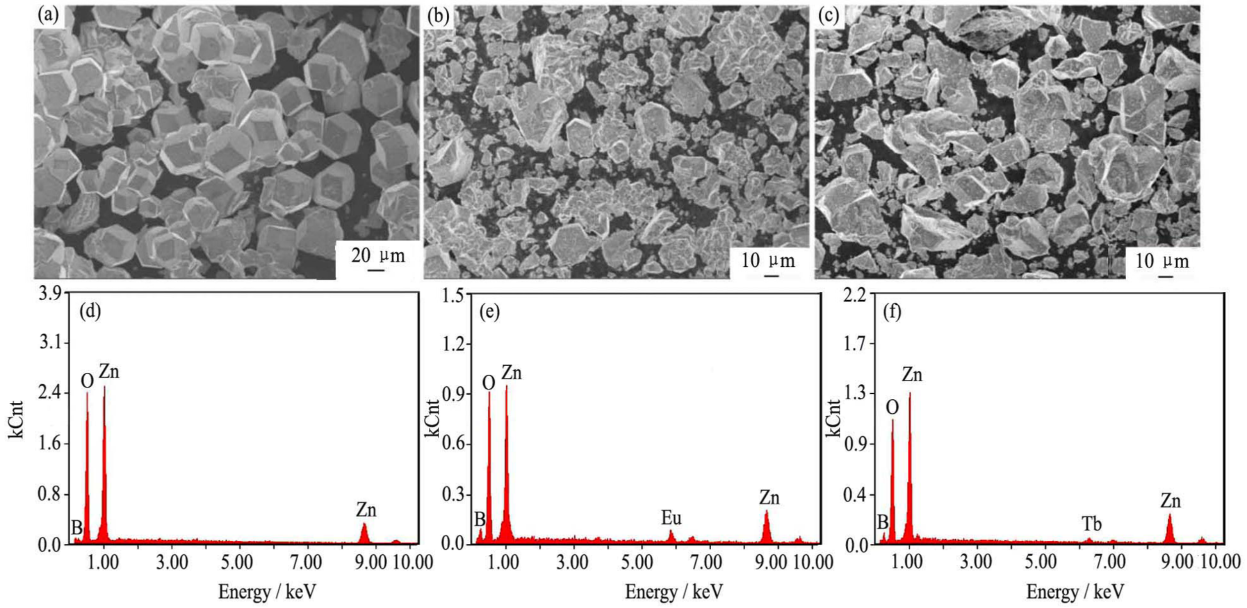

Fig. 2 SEM pattern of $Zn_4B_6O_{13}$ (a), $Zn_4B_6O_{13}$:5%Eu (b), $Zn_4B_6O_{13}$:1%Tb (c), and EDS patterns of $Zn_4B_6O_{13}$ (d), $Zn_4B_6O_{13}$:5%Eu (e) and $Zn_4B_6O_{13}$:1%Tb (f)