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Effect of Eu^{3+} contents on structure and luminescence properties of $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} and $Na_3Bi_{1-x}(PO_4)_2$:xEu^{3+} phosphors

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Abstract: A series of $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} and $Na_3Bi_{1-x}(PO_4)_2$:xEu^{3+} phosphors were successfully synthesized by solid-state method. The structure and luminescence properties were carefully investigated. The excitation spectra presented an obvious excitation band, and the peak was located at 396 nm, which matched well with the popular emissions from near-UV light-emitting diode chips. With the phase of $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} changing to that of $Na_3Bi_{1-x}(PO_4)_2$:xEu^{3+}, the intensity of magnetic dipole transition ($^5D_0 \rightarrow F_1$) at 598 nm became stronger than that of electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) at 621 nm. Under 396 nm excitation, the chromaticity coordinates and the decay curves of the entitled phosphors were also investigated. Based on all experiments without concentration quenching, we could control the luminescence intensity of the material by adjusting the doping amount of the active ions. All results indicated that $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} and $Na_3Bi_{1-x}(PO_4)_2$:xEu^{3+} phosphors have potential application as red phosphors in near UV chip-based white light emitting diodes.

Keywords: phosphors; luminescence; rare earths; optical materials; optical properties

Nowadays, white light-emitting diode (LED) is regarded as the fourth-generation light source following the incandescent, fluorescent and high intensity discharge (HID) lamps[1,2]. The research on ultraviolet or near-ultraviolet phosphors used in the LED has attracted more and more researchers. Currently, white LED generated by optical conversion can achieve industrialization. The commercial method to create white LEDs is the combination of a yellow emitting phosphor YAG:Ce^{3+} and a blue LED chip[3,4]. However, these phosphor materials exhibit a relatively poor color rendering index due to the absence of red component[5,6]. Another method for generating illumination-grade light is by blending a near-UV LED with tri-color phosphors on the chip surface[7,8]. This style also has many pleasing advantages, such as a color rendering index (CRI) of $R_a \geq 80$, fair light efficacy and stable emissions. However, available red phosphors are also inefficient[9]. To solve this problem, researchers have been looking for a suitable red phosphor. Recently, research in this area is mainly focused on silicates, molybdates, borates, phosphates and nitrides. Most of these materials have strong absorption in the short ultraviolet (UV) segment, but weak absorption in the long wavelength ultraviolet range, which does not match the UV/NUV emitting chips. Therefore, it is necessary to develop high efficient and stable red-emitting phosphors that can be excited under near-UV irradiation.

Phosphate is considered to be excellent host material because of its many favorable properties, such as low synthesis temperature, high light efficiency and stable emitting[10]. Recently, extensive attention has been gained on the development of phosphate host for luminescent materials[11]. Nagpure et al.[12] reported $Na_3Al_2(PO_4)_3$:Eu^{3+} phosphors which can be used for fluorescent lamps, PDP, and solid-state lighting devices. Wang's research group[13] reported $Ba_3Bi(PO_4)_3$:Eu^{3+} phosphor, its luminescence properties are very excellent. Based on the previous studies, our research group continues in-depth research in this area. In this study, red-emitting phosphors $Na_3Bi_2(PO_4)_3$:Eu^{3+} and $Na_3Bi(PO_4)_2$:Eu^{3+} were first synthesized by solid-state method, and it was found that $Na_3Bi_2(PO_4)_3$:Eu^{3+} could turn into $Na_3Bi(PO_4)_2$:Eu^{3+} with increasing Eu^{3+} concentration. The photoluminescence (PL) properties of the phosphors were investigated in detail. The results indicated that $Na_3Bi_2(PO_4)_3$:xEu^{3+} and $Na_3Bi(PO_4)_2$:xEu^{3+} may be useful for the development of NUV chip-based white LEDs.

1 Experimental

The phosphors were synthesized by the high-tem-

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perature solid state method. Bi_2O_3 (≥99.9%), Na_2CO_3 (≥99.9%), $(NH_4)_2HPO_4$ (≥99.9%) and Eu_2O_3 (≥99.99%) were used as the raw materials. The $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} and $Na_3Bi_{1-x}(PO_4)_2$:xEu^{3+} reactants were weighed in stoichiometric proportion, thoroughly mixed through grinding by an agate mortar and a pestle for more than 30 min. The obtained mixtures were heated at 800 ºC for 4 h and then cooled down to room temperature, and ground again into powder for measurement.

Phase formation of phosphors was determined by using powder X-ray diffraction (XRD) analysis (Bruker AXS D8 advanced automatic diffractometer, Bruker Co. Germany), with Ni-filtered Cu Kα radiation (λ=0.154178 nm). The photoluminescence (PL) spectra and luminescence decay curves were detected by a fluorescence spectrophotometer (Hitachi F-4600, Japan). The Commission International de l'Eclairage (CIE) chromaticity coordinates of sample were calculated by CIE 1931 software. Photoluminescence absolute quantum efficiency (QE) was measured by using an absolute PL quantum yield measurement system (HORIBA, FL-1057). All of the photoluminescence measurements were carried out at room temperature.

2 Results and discussion

2.1 Phase characterization

The XRD patterns of JCPDS file No. 46-0251, file No. 41-0178 and $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} (x=0.05, 0.10, 0.125, 0.15, 0.20, 0.25 and 0.30) are shown in Fig. 1. The results indicated that diffraction peaks for $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} (x=0.05, 0.10) can be indexed to orthorhombic structure and lattice parameters a=19.689 nm, b=1.072 nm, c=1.0682 nm, Z=8 and V=2.25461 nm^3, according to JCPDS No. 46-0251. Comparing the diffraction peaks with the pure phase, it can be seen that the diffraction peaks from the as-synthesized products coincide well with the $Na_3Bi_2(PO_4)_3$ structure. There is no (detectable) additional phases present. While, with increasing Eu^{3+} concentration, the XRD patterns of as-synthesized compounds $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} ($0.15<x<0.30$) are similar to JCPDS No. 41-0178 and $Na_3Bi_{1.875}(PO_4)_3$:$0.125Eu^{3+}$ is an intermediate phase, which is a transition state between $Na_3Bi_2(PO_4)_3$ and $Na_3Bi(PO_4)_2$. From the valence of chemical elements and ionic radii, we can predict that Eu^{3+} ions may be occupied by Bi^{3+} ions. Through the comparison between the phase of Eu^{3+} concentration for $0<x<0.10$ and $0.15<x<0.30$, we can determine that $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+} has a saturation value (x=0.10). With increasing doping Eu^{3+}, the powder structure changes to $Na_3Bi(PO_4)_2$ (JCPDS No. 41-0178), which may be because the increase of Eu^{3+} ions means the reduction of Bi^{3+} ions so that very few Bi^{3+} ions cannot form the phase of $Na_3Bi_2(PO_4)_3$ (JCPDS No. 46-0251).

Considering that the powder structure changes to $Na_3Bi(PO_4)_2$ with increasing Eu^{3+} concentration, we also synthesized $Na_3Bi_{1-x}(PO_4)_2$:xEu^{3+} phosphors. The X-ray powder diffraction patterns of $Na_3Bi_{1-x}(PO_4)_2$:xEu^{3+} ($0<x\leq0.30$) phosphors are shown in Fig. 2, which have orthorhombic structure and lattice parameters a=1.604 nm, b=1.856 nm, c=1.3972 nm, Z=24 and V=4.15950 nm^3, according to JCPDS No. 41-0178. The results indicate that all of the samples with different Eu^{3+} contents from 0.05 to 0.30 mol have similar diffraction patterns and no secondary phase was observed. Of course, with the larger Eu^{3+} concentration, there is a slight shift of diffraction profile toward the bigger angles, which can be attributed to the ionic size of Eu^{3+} smaller than that of Bi^{3+} to form the powder.

2.2 Luminescence properties

Fig. 3 shows the PL excitation (PLE) spectra of typical sample $Na_3Bi_{1.9}(PO_4)_3$:$0.1Eu^{3+}$ and $Na_3Bi_{1.8}(PO_4)_3$:$0.2Eu^{3+}$ monitoring at the $^5D_0\rightarrow{}^7F_2$ emission (621 nm). The PLE spectra of $Na_3Bi_2(PO_4)_3$:Eu^{3+} clearly shows a week absorption band from 220 to 350 nm and several excitation bands. The week band extending from 200 to 350 nm of

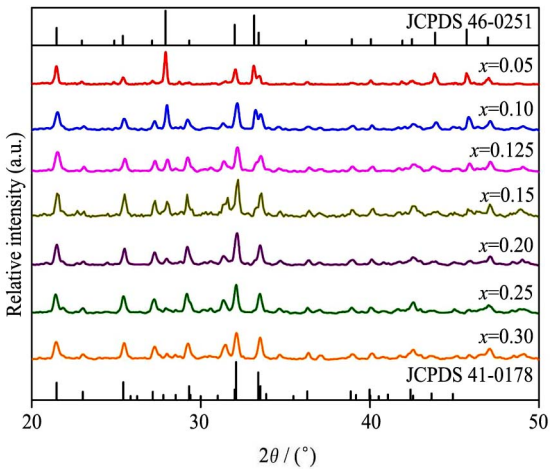

Fig. 1 XRD patterns of JCPDS $Na_3Bi_{2-x}(PO_4)_3$:xEu^{3+}, JCPDS No. 46-0251 and No. 41-0178

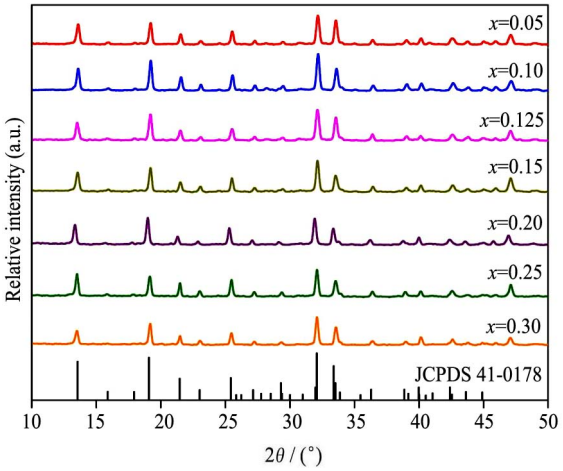

Fig. 2 XRD patterns of $Na_3Bi_{1-x}(PO_4)_3$:xEu^{3+} and JCPDS No. 41-0178