A Novel Blue-green-emitting Phosphor $LiBaPO_4:Eu^{2+}$ for White Light-emitting Diodes

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A novel efficient blue-green-emitting phosphor, $LiBaPO_4:Eu^{2+}$, was prepared by solid-state reaction method. Its excitation band is extending from 250 to 450 nm, which is adaptable to the emission band of near-ultraviolet (NUV) LED chips (350–420 nm). Upon 348-nm light excitation, the phosphor exhibits a strong blue-green emission peaking at 480 nm. A bright blue-green LED was fabricated by incorporating the phosphor with an InGaN-based NUV chip. All the characteristics suggest that $LiBaPO_4:Eu^{2+}$ is a good blue-green phosphor candidate for creating white light in phosphor-converted white LEDs.

There is an increasing demand for white light-emitting diodes (WLEDs) as potential replacement for the incandescent and fluorescent light sources because of their high luminous efficiency, energy-saving, maintenance, and environment protection.[1–3] Recently, remarkable progress has been made in the development of (Al, In)GaN chips with emission bands shifted to near-ultraviolet (NUV) range (350–420 nm).[2] Compared with the currently commercial WLED fabricated with a blue chip and a yellow phosphor $YAG:Ce^{3+}$, the WLED fabricated with an NUV chip around 350–420 nm and corresponding phosphors has higher color-rendering index[3–6] because all the colors are determined by the phosphors. Therefore, the wavelength conversion phosphor materials play a crucial role in solid-state lighting innovation. An important new development in the field of luminescent materials is the search for ideal/suitable phosphors for the conversion of the NUV emission from InGaN chips into visible light.

The compounds $ABPO_4$ ($A = Li^+$, Na^+, K^+, Rb^+, and Cs^+; $B = Sr^{2+}$ and Ba^{2+}) show excellent thermal and hydrolytic stability and were considered to be efficient luminescent hosts.[7–14] Recently, two novel blue-emitting phosphors, $LiSrPO_4:Eu^{2+}$ and $KSrPO_4:Eu^{2+}$,[15,16] for WLEDs were also reported. However, to the best of our knowledge, there is no report on the research of $LiBaPO_4:Eu^{2+}$ for potential application as a blue-green phosphor. In this letter, a novel blue-green-emitting phosphor, Eu^{2+}-doped $LiBaPO_4$, was synthesized by solid-state reaction method, and the photoluminescence properties of the phosphor were investigated. Finally, blue-green LED was fabricated by combining an NUV InGaN chip ($\lambda_{em} = 373$ nm) with the phosphor.

$LiBa_{1-x}PO_4:Eu^{2+}{}_x$ ($x = 0.01$–0.09) phosphors were synthesized by a conventional solid-state reaction technique. The starting materials Li_2CO_3 (AR), $BaCO_3$ (AR), $NH_4H_2PO_4$ (AR), and Eu_2O_3 (99.99%) with stoichiometric molar ratio were firstly ground and then heated in an electric furnace at 1200 °C for 3 h under a reducing CO atmosphere. Crystal phase identification was carried out on an X-ray diffractometer (D/max-IIIA, RIGAKU Corporation of Japan) using 40 kV, 20 mA and Cu Kα radiation (1.5406 Å). Excitation and emission spectra of the powdered phosphors were measured on a Fluorolog-3-21 spectrometer (JOBIN YVON, America) at room temperature, and a 450-W Xenon lamp was used as the excitation source. The emission spectra of the LEDs were recorded on a PMS-50 LED spectrophotocolorimeter (EVERFINE, China).

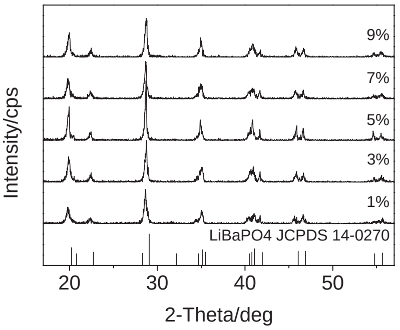

Figure 1. XRD patterns of $LiBa_{1-x}PO_4:Eu^{2+}{}_x$ ($x = 0.01$–0.09).

The XRD patterns of the samples, $LiBa_{1-x}PO_4:Eu^{2+}{}_x$ ($x = 0.01$–0.09), are shown in Figure 1. All the diffraction peaks can be indexed to the phases of $LiBaPO_4$ (JCPDS 14-0270), which has been refined to be orthorhombic with the cell parameters of $a = 8.633$, $b = 8.735$, and $c = 5.211$ Å.[14] The result indicates that the doped Eu^{2+} ions have little influence on the crystalline structure of phosphors.

Figure 2 is the photoluminescence spectra of the obtained $LiBa_{0.95}PO_4:Eu^{2+}{}_{0.05}$ phosphor. A broad excitation band ranging from 250 to 440 nm is observed, which means this phosphor may be suitable for application to white LEDs excited by NUV light. Since the host $LiBaPO_4$ hardly shows any absorption between 250 and 440 nm, the excitation band is attributed to the transition from $4f^7$ ground state to the excited sate $4f^65d^1$ of the doped Eu^{2+} ions. Under 348 nm NUV-light excitation, the $LiBa_{0.95}PO_4:Eu^{2+}{}_{0.05}$ phosphor shows intense broad blue-green emission peaking at 480 nm with the full width at half-maximum (fwhm) of 86 nm. The emission spectrum can be attributed to the typical $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions. No emission peaks of Eu^{3+} were observed in the spectra, indicating that Eu^{3+} ions in the matrix have been reduced to Eu^{2+} completely under the reducing CO atmosphere. The effect of doped Eu^{2+} concentration on the emission of $LiBaPO_4:Eu^{2+}$ phosphor was also investigated. The critical quenching concentration of Eu^{2+} in $LiBaPO_4:Eu^{2+}$ phosphor is about 5 mol % (Figure 3).

In order to investigate the luminescent properties of the phosphor in NUV LED, a blue-green LED was fabricated by combination of an NUV InGaN chip and the prepared $LiBaPO_4:Eu^{2+}$ phosphor. The emission spectrum of the LED under 20 mA forward bias excitation is shown in Figure 4. A very broad emitting band peak at 480 nm, attributed to the

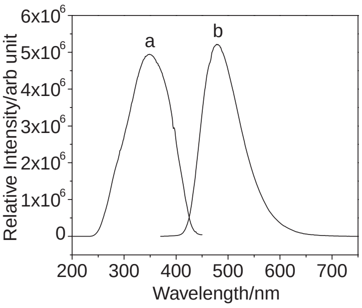

Figure 2. Photoluminescence spectra of $LiBa_{1-x}PO_4{:}Eu^{2+}{}_x$: (a) excitation spectrum ($\lambda_{em} = 480\,nm$), (b) emission spectrum ($\lambda_{ex} = 348\,nm$).

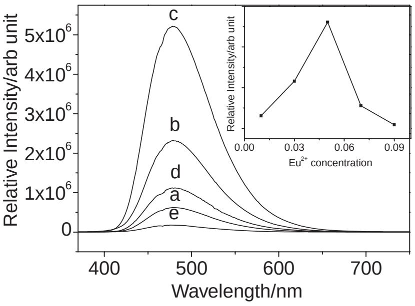

Figure 3. The emission spectra of $LiBa_{1-x}PO_4{:}Eu^{2+}{}_x$ with varying Eu^{2+} concentrations (a: $x = 0.01$, b: $x = 0.03$, c: $x = 0.05$, d: $x = 0.07$, e: $x = 0.09$)($\lambda_{ex} = 348\,nm$).

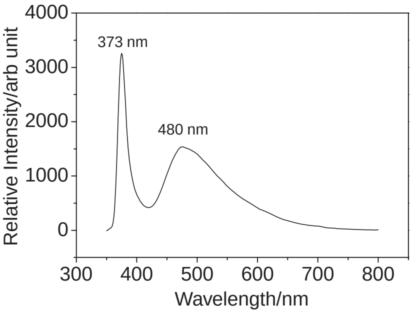

Figure 4. Emission spectrum of the LED with $LiBa_{0.95}PO_4{:}Eu^{2+}{}_{0.05}$ phosphor under a forward bias of 20 mA.

Eu^{2+} emission of $LiBa_{0.95}PO_4{:}Eu^{2+}{}_{0.05}$, appears under the near UV-light excitation from the InGaN chip while the 373-nm emission peak from the chip itself partly remains. It is important that the remained NUV bands are still quite intense, thus other color phosphor can also be excited by cocoating with the blue-green $LiBaPO_4{:}Eu^{2+}$ phosphor onto the same chip to create white light.

A photograph of the lighting blue-green LED with $LiBa_{0.95}PO_4{:}Eu^{2+}{}_{0.05}$ is shown in Figure 5. Bright blue-green light from the LED is observed by naked eyes, and its CIE chromaticity coordinates are calculated as ($x = 0.2350$, $y = 0.3253$). In views of application, each proper LED phosphor must meet the following necessary conditions. Firstly, the phosphor should efficiently absorb NUV light emitted from the InGaN chip. Then, the phosphor exhibits higher luminescent intensity under NUV light excitation. Since $LiBaPO_4{:}Eu^{2+}$ meets both the conditions, it is considered to be a potential candidate as a blue-green component for fabrication of white LEDs.

Figure 5. The photograph of $LiBa_{0.95}PO_4{:}Eu^{2+}{}_{0.05}$–InGaN LED under 20-mA current excitation.

In conclusion, a novel blue-green phosphor $LiBaPO_4{:}Eu^{2+}$ was prepared by the high-temperature solid-state reaction, and a bright blue-green LED with CIE chromaticity coordinates of ($x = 0.2350$, $y = 0.3253$) was fabricated by incorporating the phosphor with InGaN-based NUV chip. All the characteristics indicate that $LiBaPO_4{:}Eu^{2+}$ is a good candidate phosphor applied in white LEDs.

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