Synthesis and luminescence properties of Eu$^{2+}$-activated phosphor Ba$_3$Lk(PO$_4$)$_3$F for n-UV white-LEDs

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**Abstract**

The simple high-temperature solid-state route was adopted to synthesize a series of related Ba$_3$Lk(PO$_4$)$_3$F:$x$Eu$^{2+}$ (BLKPF:$x$Eu$^{2+}$) blue phosphors. The photoluminescence (PL) and diffuse reflection spectra have been investigated in detail. These phosphors which can be well excited by the 388 nm near-ultraviolet light, produce the emitted blue light peaks located at about 460 nm. The critical Eu$^{2+}$ concentration quenching mechanism was ascribed to the dipole–dipole interaction, and the optimum concentration was eventually proved to be 0.1 mol. All above results indicate that Ba$_3$Lk(PO$_4$)$_3$F:$x$Eu$^{2+}$ phosphor can act as an appropriate candidate of the blue phosphor in the future.

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**1. Introduction**

Under the background of global energy shortage, white light emitting diodes (W-LEDs) was called the fourth generation lighting source and has been widely applied owing to its excellent properties, such as environmentally-friendly, energy saving, low-consumption, highly-efficiency and so on [1–4]. One method to generate the practical white light emission was to combine tricolor phosphors with a n-UV-InGaN chips (350–420 nm) [5–7]. Among tricolor phosphors, the blue component occupies a large proportion, so it is meaningful to explore blue-emitting phosphors for the development of w-LEDs.

Since light-emitting wavelength of the chips available in the market are most at 350–420 nm which locates at n-UV region, it is important to explore phosphors that can be excited by the n-UV optical source [8–11]. Phosphor consists of activator and matrix; as a super activator, Eu$^{2+}$ ions can generate blue spectra with 4f$^6$–5d transition and have been intensely studied among the rare earth family [12–14]. Beyond this, good phosphors also need an appropriate substrate. Apatite is an excellent substrate because of its good chemical stability and it can be formulated as $A_{10}[PO_4]_6Z_2$; $A$ often represents divalent cations such as Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Mn$^{2+}$ and Pb$^{2+}$; $Z$ is denoted by $F^-$, $Cl^-$, $OH^-$, or $O^{2-}$ [15,16]. Apatite compounds have been widely investigated in many fields for various applications, such as Sr$_5$(PO$_4$)$_2$SiO$_4$, Ca$_5$–PO$_4$$_2$SiO$_4$ [17–20] and so on. To enrich its applications, apatite needs more forms and there are many opportunities to build up new inorganic framework to obtain new compounds with apatite structure since it possesses wide accommodation ability in $A$ sites [21–25]. The more the frameworks are, the more selections do the engineers have. Up to now, there is no report about Eu$^{2+}$-doped Ba$_3$Lk(PO$_4$)$_3$F phosphor with an apatite structure [26–29].

In this study, a series of new Ba$_3$Lk(PO$_4$)$_3$F:$x$Eu$^{2+}$ phosphors with apatite structure have been reported, and their photoluminescence properties have been discussed in detail. The synthesis technique with a relative low temperature and reductive atmosphere provided by CO requires low energy consumption and is easy to achieve compared to the phosphors which must be prepared at high temperature and under high pressure. According to all these results, the phosphor could have potential application in the n-UV-wLEDs as blue components.

**2. Experimental**

A sequence of phosphors Ba$_3$Lk(PO$_4$)$_3$F:$x$Eu$^{2+}$ were set by the conservative high-temperature solid-state method. The fresh materials were (NH$_4$)$_2$HPO$_4$ (A.R.), BaCO$_3$ (A.R.), K$_2$CO$_3$ (A.R.), NH$_4$–HF$_2$ (A.R.), La$_2$O$_3$ (99.99%), and Eu$_2$O$_3$ (99.99%), which were used immediately without any handling. X-ray diffraction patterns (Cu Kα line, 40 kV, 30 mA) with radiation ($\lambda = 0.15406$ nm) were obtained using an X-ray powder diffractometer (XD-3, PGENERAL,
3. Results and discussions

We adopted XRD analysis to verify structures of the as-setted samples. As shown in Fig. 1, the representative XRD patterns include the Ba$_3$LaK(PO$_4$)$_3$F and the Ba$_3$LaK(PO$_4$)$_3$F:0.1Eu$^{2+}$ phosphor. It is obvious that the XRD patterns of them can be matched perfectly to the phase of Ba$_3$LaNa(PO$_4$)$_3$F (JCPDS No. 71-1337), which belongs to apatite structure with the hexagonal system and the group space $P6_3/m$. In view of the positions and intensities of diffraction peak matched well with the reference JCPDS file, we can see that the doping caused by Eu ions did not bring about variation in the structure, which indicates the successful isomorphic replacement of Eu atoms to Ba atoms and K atoms to Na atoms in the present structure [30].

We measured the important spectra of different samples to evaluate the application value of the phosphor which has an apatite structure. Fig. 2 depicts the photoluminescence excitation (PLE), photoluminescence emission (PL) and the diffuse reflection spectra of the Ba$_3$LaK(PO$_4$)$_3$F:0.1Eu$^{2+}$ phosphor. (Color online.) We adopted XRD analysis to verify structures of the as-setted samples. As shown in Fig. 1, the representative XRD patterns include the Ba$_3$LaK(PO$_4$)$_3$F and the Ba$_3$LaK(PO$_4$)$_3$F:0.1Eu$^{2+}$ phosphor. It is obvious that the XRD patterns of them can be matched perfectly to the phase of Ba$_3$LaNa(PO$_4$)$_3$F (JCPDS No. 71-1337), which belongs to apatite structure with the hexagonal system and the group space $P6_3/m$. In view of the positions and intensities of diffraction peak matched well with the reference JCPDS file, we can see that the doping caused by Eu ions did not bring about variation in the structure, which indicates the successful isomorphic replacement of Eu atoms to Ba atoms and K atoms to Na atoms in the present structure [30].

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![Fig. 1. XRD patterns of Ba$_3$LaK(PO$_4$)$_3$F and Ba$_3$LaK(PO$_4$)$_3$F:0.1Eu$^{2+}$ samples. The standard data for Ba$_3$LaNa(PO$_4$)$_3$F (JCPDS No. 71-1317) is also shown as a reference.](image1)

![Fig. 2. Photoluminescence excitation (PLE, left) spectra, photoluminescence emission (PL, right) and diffuse reflection spectra (blue) of Ba$_3$LaK(PO$_4$)$_3$F:0.1Eu$^{2+}$ phosphor. (Color online.)](image2)
coordinate is calculated to be (0.147, 0.092), which means that the phosphor can be used as a blue-emitting phosphor for w-LEDs application. Meanwhile, the typical digital photo of the Ba2.9LaK(PO4)3F:0.1Eu2+ phosphor under 365 nm UV lamp is shown in the inset of Fig. 4, and the blue light emission can be seen by naked eyes.

All the results above prove that Ba3LaK(PO4)3F:xEu2+ phosphors with 4f–5d absorption efficiency in n-UV region can play an important role in blue emitting phosphor and are potentially useful for C24 370 nm GaN-based w-LEDs.

4. Conclusions

In summary, blue phosphor Ba3LaK(PO4)3F:xEu2+ was acquired via conservative high-temperature solid-state method. The phosphor showed the emitted blue light peaks locate at about 460 nm ascribed to the 4f–5d transition of Eu2+. It was further proved that concentration quenching of Eu2+ ions in Ba3LaK(PO4)3F:0.1Eu2+ phosphors resulted from the dipole–dipole interactions. All the spectrum features indicate that this blue phosphor might be a component for w-LEDs.

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References