Improving the luminescence properties of $Ba_3Eu(PO_4)_3$ by doping Sm^{3+} as sensitizer*

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For enhancing the emission intensity and broadening the excitation region of $Ba_3Eu(PO_4)_3$ (BEP), Sm^{3+} is doped as sensitizer in this paper. BEP:Sm^{3+} can produce an obvious red emission at near ultraviolet (n-UV) radiation. An effective energy transfer from Sm^{3+} to Eu^{3+} is proved. The commission international de I'Eclairage (CIE) chromaticity coordinates of BEP:Sm^{3+} locate at red region. When the environment temperature is 150 °C, the emission intensity of BEP:0.10Sm^{3+} is decreased to 76% of the initial one at room temperature, and the activation energy is calculated to be 0.164 eV, which can prove the good thermal stability of BEP:Sm^{3+}. The results indicate that BEP:Sm^{3+} may have potential applications in white light emitting diodes (LEDs).

Recently, in order to achieve high color rendering index (*CRI*) and high correlated color temperature (*CCT*) white light emitting diodes (LEDs), an alternative method, a combination of near-ultraviolet (n-UV) or ultraviolet (UV) LED with red, green and blue emitting phosphors, has been developed[1-3]. However, one of the key factors limiting the progress of white LEDs is the general lack of red emitting phosphors, which will limit the performance of white light blends in terms of color rendering and lumen equivalency[4]. Generally, the Eu^{3+} ion has been recognized as an excellent activator in red phosphors due to the $^5D_0$-^7F_J (J=0, 1, 2, 3, 4) transitions of Eu^{3+}[5-7], but this kind of phosphors may have a weak absorption in the n-UV region. Therefore, to overcome this drawback, a host lattice with high concentration of Eu^{3+}, without causing serious concentration quenching, is needed. For example, Xia et al[8] reported the luminescence properties of $Ba_3Eu(PO_4)_3$ (BEP). Actually, the luminescence properties of Eu^{3+} doped phosphors can also be improved by introducing sensitizers[9-12]. Therefore, in order to obtain a high-efficiency red phosphor, we select BEP as host and introduce Sm^{3+} as sensitizer to improve the luminescence properties. The results may be useful for the development of red phosphors.

$BaCO_3$ (analytical reagent, A. R.), $NH_4H_2PO_4$ (A. R.), Sm_2O_3 (99.99%) and Eu_2O_3 (99.99%) were used as the raw materials. A series of BEP, $Ba_3Eu_{1-x}(PO_4)_3$:xSm^{3+} samples were synthesized by a high temperature solid-state method. The stoichiometric amount of raw materials was thoroughly mixed and ground by an agate mortar and pestle for more than 30 min till they were uniformly distributed, and the obtained mixtures were heated at 1 150 °C for 4 h in air. Then the obtained samples were cooled to room temperature and ground again in an agate mortar.

Phase formation of phosphors was carefully checked by powder X-ray diffraction (XRD) analysis using Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu Kα1 radiation (λ=0.154 05 nm) operating at 40 kV and 40 mA, and a scan rate of 0.02 °/s was applied to record the patterns in the 2θ range from 10° to 70°. Luminescence spectra and decay curves were detected by an FLS920 fluorescence spectrometer with the scanning wavelength range from 200 nm to 700 nm and a spectral resolution of 0.2 nm, and the exciting source was a 450 W Xe lamp. Commission international de I'Eclairage (CIE) chromaticity coordinates of sample were measured by a PMS-80 spectra

analysis system. All measurements were carried out at room temperature. High-temperature photoluminescence spectra were detected by the Hitachi F-4600 with a TAP-02 high temperature control system with the scanning wavelength range from 400 nm to 700 nm and a spectral resolution of 0.2 nm, and the exciting source was a 450 W Xe lamp.

Fig.1 shows the XRD patterns of BEP:xSm^{3+} (x=0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10). All the diffraction peaks match well with those of the cubic Ba$_3$Bi(PO$_4$)$_3$ according to the standard reference of JCPDS card No.33-0137, and no trace of impurity phase is observed. The results indicate little change of this crystal structure when introducing Sm^{3+} ions into BEP. According to JCPDS card No.33-0137, BEP should belong to the eulytite-type compounds which crystallize in the cubic system with space group I-43d.
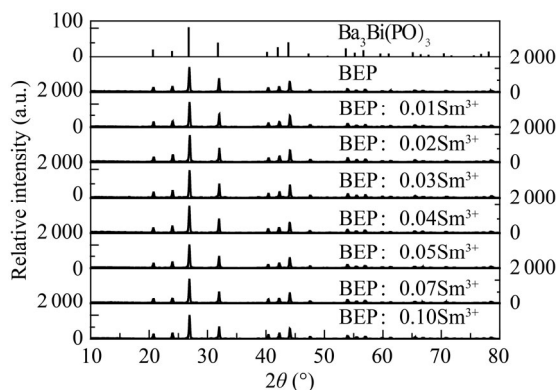

Fig.1 XRD patterns of BEP and BEP:xSm^{3+} with the standard data of Ba₃Bi(PO₄)₃

Figs.2 and 3 present the excitation and emission spectra of BEP and BEP:0.10Sm^{3+}. Comparing the excitation spectrum of BEP with that of BEP:0.10Sm^{3+}, Fig.2 shows that there are some differences. For example, for 603 nm and 615 nm emission peaks of BEP:0.10Sm^{3+}, the corresponding excitation not only shows a weak broad band ranging from 200 nm to 280 nm and some narrow peaks (287 nm, 297 nm, 319 nm, 362 nm, 382 nm, 393 nm, 415 nm, 444 nm and 465 nm) resulting from the combined absorption of host and Eu^{3+}-O^{2-} charge transfer (CT) transition, as well as 4f-4f characteristic transitions of Eu^{3+}, but also depicts an obvious excitation peak of Sm^{3+} which is labeled by the dash line. Moreover, in the region of 395—410 nm, the excitation intensity is obviously enhanced, which locates between the dash dot lines. On the other hand, Fig.3 shows that BEP and BEP:0.10Sm^{3+} present the same spectral distribution at different excitation radiations, and there is no obvious emission peak of Sm^{3+}[13]. However, the emission intensity of BEP:0.10Sm^{3+} is obviously stronger than that of BEP. The above results indicate that there may be the energy transfer from Sm^{3+} to Eu^{3+} in BEP:Sm^{3+}.
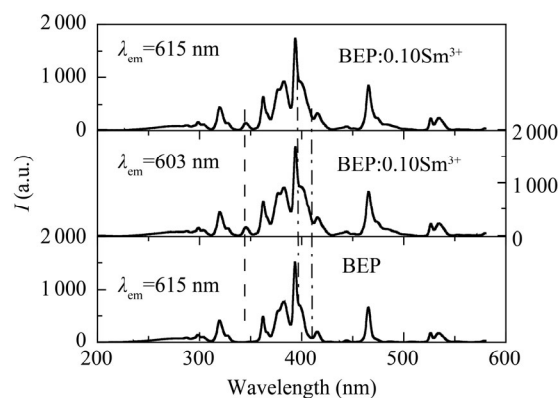

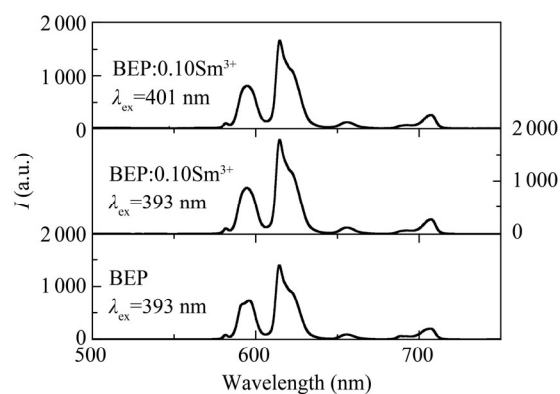**Fig.2 Excitation spectra of BEP and BEP:0.10Sm^{3+}**

Fig.3 Emission spectra of BEP and BEP:0.10Sm^{3+}

As shown in Fig.3, although there is no emission peak of Sm^{3+}, we can measure the decay curves of Eu^{3+} to further validate the process of energy transfer from Sm^{3+} to Eu^{3+}. Fig.4 presents the decay curves of Eu^{3+} peak at 615 nm (λ_{ex}=393 nm) with different concentrations of Sm^{3+}, and all samples show a nearly single-exponential decay trend, which can be described as[14]

$$I=I_0\exp(-t/\tau), \tag{1}$$

where I_0 and I are intensities at moments of 0 and t, respectively, and τ is the lifetime for transition. There is a more and more quick decline with the increasing concentration of Sm^{3+}. The above results illustrate two points: with increasing the concentration of Sm^{3+} (x=0—0.10), the Eu^{3+} content is dropped from 1 to 0.9, however, the emission intensity of Eu^{3+} is enhanced, so there is no concentration quenching effect of BEP; the increase of emission intensity of Eu^{3+} should only be caused by the energy transfer from Sm^{3+} to Eu^{3+}.

For application, the thermal stability of phosphor is one of the important issues to be considered. The emission intensities of BEP:0.10Sm^{3+} at different temperatures are shown in Fig.5(a). The results show that the intensity of sample drops to about 81.0% when temperature is 150 °C. The activation energy (E_a) can be expressed as[15]

$$\ln(I_0/I)=\ln A-E_a/kT, \qquad (2)$$

where I_0 and I are luminescence intensities of BEP: $0.10Sm^{3+}$ at room temperature and the testing temperature T, respectively. A is a constant, and $k=8.617\times10^{-5}$ eV·K^{-1} is the Boltzmann constant. As shown in Fig.5(b), the activation energy ΔE is achieved as 0.164 eV. The above results indicate that the BEP:$0.10Sm^{3+}$ has a good thermal stability.
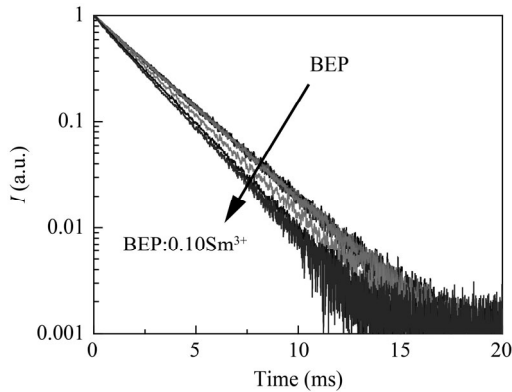

Fig.4 Decay curves of BEP:xSm^{3+} (x=0—0.10, λ_{ex}=393 nm, λ_{em}=615 nm)

the performance of phosphors. Tab.1 depicts the commission international de I'Eclairage (CIE) 1931 chromaticity coordinates of BEP:xSm^{3+}. The results show that the CIE chromaticity coordinates of BEP:xSm^{3+} all locate at red region, such as BEP (0.653 1, 0.353 9), which are quite close to those of commercial red phosphors $Sr_2Si_5N_8$:Eu^{2+} (0.620, 0.370) and Y_2O_2S:Eu^{3+} (0.622, 0.351). The results mean that BEP:xSm^{3+} may serve as potential red or orange-red emitting materials for n-UV based white LEDs.

Tab.1 CIE chromaticity coordinates of $Ba_3Eu_{1-x}(PO_4)_3$: xSm^{3+} (x=0—0.10) (λ_{ex}=365 nm)

$Ba_3Eu_{1-x}(PO_4)_3$:xSm^{3+}	CIE (X, Y)
x=0	(0.653 1, 0.353 9)
x=0.01	(0.645 1, 0.353 7)
x=0.02	(0.637 9, 0.354 1)
x=0.03	(0.645 7, 0.352 8)
x=0.04	(0.644 7, 0.353 4)
x=0.05	(0.646 3, 0.354 2)
x=0.07	(0.645 4, 0.353 2)
x=0.10	(0.653 4, 0.354 2)

A series of BEP and BEP:Sm^{3+} were synthesized by the high temperature solid-state method. The emission intensity and excitation intensity of BEP can be enhanced by the efficient energy transfer from the sensitizer Sm^{3+} to Eu^{3+}, and the results are proved by the spectral characteristics and decay curves. BEP:Sm^{3+} shows an obvious red emission, and the CIE chromaticity coordinates are quite close to those of commercial red phosphors $Sr_2Si_5N_8$:Eu^{2+} and Y_2O_2S:Eu^{3+}. BEP has a good thermal stability, and the activation energy is 0.164 eV. The results indicate that BEP:Sm^{3+} may have the potential applications in white LEDs.

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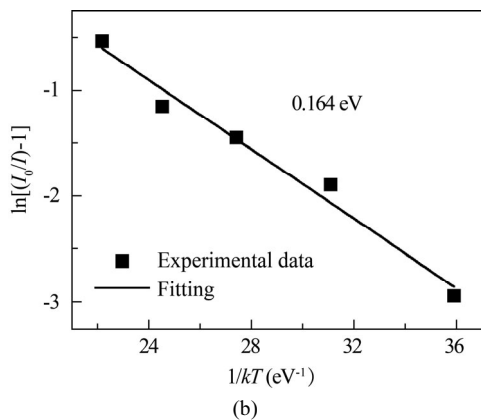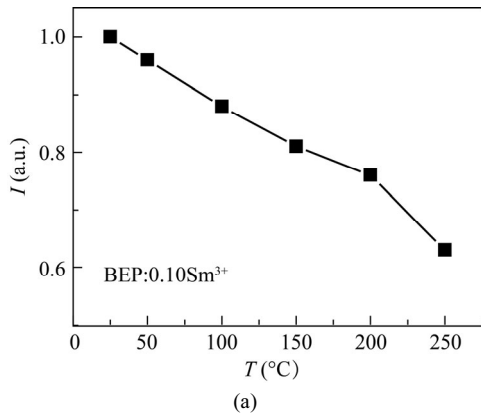
Fig.5 (a) Emission intensity of BEP:$0.10Sm^{3+}$ as a function of temperature (25—250 °C); (b) Arrhenius fitting of emission intensity of BEP:$0.10Sm^{3+}$ and the activation energy (ΔE) for thermal quenching

Generally, color coordinates can be used for evaluating

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