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Tunable luminescence properties and efficient energy transfer in Eu^{2+}, Tb^{3+} co-doped $NaBaPO_4$

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ABSTRACT

Eu^{2+} and Tb^{3+} singly doped and co-doped $NaBaPO_4$ phosphors were synthesized by solid state reaction. The structure character, photoluminescence properties and the lifetime were investigated. The emission spectra of $NaBaPO_4$:Eu^{2+}, Tb^{3+}, Na^+ phosphor show both broad blue emission band and sharp green emission peaks. The energy transfer mechanism from Eu^{2+} to Tb^{3+} in $NaBaPO_4$ host was discussed. The excitation spectra of $NaBaPO_4$: Eu^{2+}, Tb^{3+}, Na^+ phosphor show broad excitation band in the 250–400 nm range, which was in agreement with the near-ultraviolet (n-UV) chip. The hue of the $NaBaPO_4$: Eu^{2+}, Tb^{3+}, Na^+ phosphors could be appropriately tuned by adjusting the contents of activators.

1. Introduction

Recently, increasing attention has been focused on the research in phosphor converted-white LEDs (pc-WLEDs) [1]. The most common way to obtain WLEDs is the combination of blue LED chips and yellow YAG: Ce^{3+} phosphors [2]. However, the deficiencies of this method are low color rendering index (CRI) (Ra < 80) and high correlated color temperature (CCT > 5000 K), due to the lack of red light emission [3–5]. Another way to generate white light is to combine n-UV LED chips with tricolor phosphors [6]. This strategy can provide improved CRI, stable chromaticity, tunable CCT and good color tolerance to chip's variation [7,8]. However, the reabsorption of emission colors, complicated manufacture and different aging rates for each phosphor will lead to the high cost and low efficiency [9,10]. Thus, a single-phased double or multi-color emitting phosphor by n-UV excitation is required to enhance the luminous efficiency and color reproducibility in the design of WLED. One of the strategies for generating single-phased emission-tunable phosphor is by co-doping sensitizer and activator into the same host, which is based on the mechanism of energy transfer. Energy transfer between Ce^{3+}/Tb^{3+} [11] and Eu^{2+}/Mn^{2+} [12] has been extensively investigated in a different host lattice. However, energy transfer from Eu^{2+} to Tb^{3+} is rarely reported [13]. In this paper, the Eu^{2+}, Tb^{3+} and Eu^{2+}/Tb^{3+} co-doped $NaBaPO_4$ (NBP) phosphor were prepared by conventional solid state reaction, the photoluminescence properties and energy transfer mechanism of NBP: Eu^{2+}, Tb^{3+}, Na^+ phosphor were discussed in detail.

2. Experimental

A series of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25) and NBP: $0.1Tb^{3+}$, $0.1Na^+$ phosphors were synthesized by a solid state reaction technology. The starting materials $NaCO_3$ (A.R.), $BaCO_3$ (A.R.), $NH_4H_2PO_4$ (A.R.), Tb_4O_7 (99.99%) and Eu_2O_3 (99.99%) were weighed in stoichiometric amounts and thoroughly mixed by grinding in an agate mortar. The Na^+ was added in NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+(x = 0.05, 0.10, 0.15, 0.20, 0.25) and NBP: $0.1Tb^{3+}$, $0.1Na^+$ as a charge compensator because the substitution of Tb^{3+} ion for a Ba^{2+} ions requires the presence of a charge compensator to maintain the overall charge neutrality of the crystal. The mixture was pre-fired at 600 °C for 1 h under air atmosphere and sintered at 1100 °C for 6 h under (75% N_2 + 25% H_2) atmosphere.

The phase purity of the as-prepared phosphors was investigated by using X-ray powder diffraction (XRD) spectroscopy with a Rigaku D/max 2200 vpc Diffractometer with Cu Kα radiation at 40 kV and 30 mA. The XRD patterns were collected in the range $10° \leqslant 2\theta \leqslant 80°$.

The excitation and emission spectra were measured by a Hitachi F7000 spectrofluorometer at room temperature. The decay curves were measured by a FLS920-Combined Fluorescence Lifetime and Steady State Spectrometer (Edinburgh Instruments).

3. Results and discussion

The XRD patterns of NBP: $0.1Tb^{3+}$, $0.1Na^+$ and NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25) phosphors are shown in Fig. 1. The results indicate that all the peaks of these phosphors

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match well with JCPDS 33-1210. Some weak peaks (∗) are due to the minor impurity $Na_4P_2O_7$ phase.

The excitation and emission spectra of NBP: $0.015Eu^{2+}$ are shown in Fig. 2(a). It is observed that the excitation spectrum consists of two broad bands at around 270 and 310 nm. Since the excitation spectra are not well resolved, the position of the lowest 5d excited level of Eu^{2+} is generally estimated to be $\sim28,818\ cm^{-1}$ by using the mirror–image relationship between the emission and the excitation spectra. The emission spectrum consists of a broad band with a maximum at about 436 nm due to the 5d–4f transitions of Eu^{2+} ion in $NaBaPO_4$ [14].

Fig. 2(b) shows the excitation and emission spectra of NBP: $0.10Tb^{3+}$, $0.10Na^+$. The emission spectrum consists of four major emission bands at around 488, 643, 583 and 623 nm attributing to the typical $^5D_4$–^7F_J ($J = 6, 5, 4, 3$) transitions of Tb^{3+} ions, respectively. Also the weak blue emission peaks at around 377, 417 and 436 nm were observed originating from the $^5D_3$–^7F_J ($J = 6, 5, 4$) transitions of Tb^{3+} ions, respectively. The excitation spectrum consists of two parts, one in the range of 250–290 nm consisting of a strong band at 265 nm and a weak band at 280 nm, which are assigned to the spin-forbidden and spin-allowed components of $4f^8$–$4f^75d^1$ transition of Tb^{3+} ion, respectively, the other sharp peak in the range of 300–500 nm is corresponding to the 4f–4f transition of Tb^{3+} ion. Though there is some absorption bands between 300 and 400 nm, the optical absorption transitions are parity–forbidden transition and the absorption intensity is very weak. So the Tb^{3+} singly doped sample cannot be efficiently excited by n-UV (350–410 nm) LED chip.

As shown in Fig. 2(a) and (b), significant spectra overlap can be observed by comparing the emission band of NBP: $0.015Eu^{2+}$ with the excitation band of NBP: $0.10Tb^{3+}$, $0.10Na^+$. Therefore, the effective resonance type energy transfer from Eu^{2+} to Tb^{3+} in $NaBaPO_4$ host can be expected to occur.

The excitation and emission spectra of NBP: $0.015Eu^{2+}$, $0.10Tb^{3+}$, $0.10Na^+$ are shown in Fig. 2(c). The emission spectra of NBP: $0.015Eu^{2+}$, $0.10Tb^{3+}$, $0.10Na^+$ exhibit the broad blue emission band centered at 436 nm due to the 5d–4f transition of Eu^{2+} ion and the sharp green emission peaks due to the 4f–4f transition of Tb^{3+} ion. The profile of the excitation spectrum under 543 nm emission of Tb^{3+} is similar to that under 436 nm emission of Eu^{2+}, which gives proof for the energy transfer from Eu^{2+} to Tb^{3+} in $NaBaPO_4$ host. The excitation band of Eu^{2+}, Tb^{3+} co-doped NaBaPO4 phosphor extends from 250 to 400 nm, which is expected
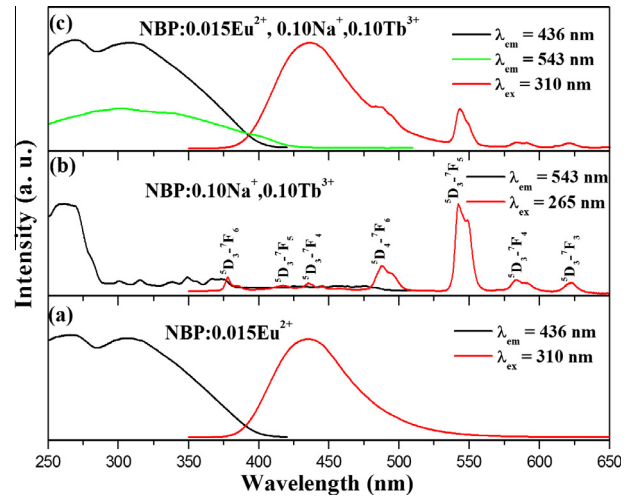

Fig. 2. Excitation and emission spectra of NBP: $0.015Eu^{2+}$ (a), NBP: $0.1Tb^{3+}$, $0.1Na^+$ (b) and NBP: $0.015Eu^{2+}$, $0.1Tb^{3+}$, $0.1Na^+$ (c).

that NBP: $0.015Eu^{2+}$, $0.10Tb^{3+}$, $0.10Na^+$ can match well with the n-UV (350–410 nm) light from InGaN based LEDs.

In order to investigate the energy transfer process involved in NBP: Eu^{2+}, Tb^{3+} phosphor, a series of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25$) phosphors were prepared. The emission spectra of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25$) phosphors under 310 nm excitation are present in Fig. 3. The intensity of Eu^{2+} emission decreases degradedly with increasing Tb^{3+} concentration from $x = 0$ to 0.25, owing to the enhancement of energy transfer from Eu^{2+} to Tb^{3+}. Meanwhile, the emission intensity of Tb^{3+} simultaneously increases with Tb^{3+} concentration.

Furthermore, the decay curves of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ phosphors were measured and shown in Fig. 4. The decay curves of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ phosphors show fast decay at the initial stage and slow decay curves at the later time region. The decay curves of all the samples are well fitted with a second-order exponential decay mode by the following equation [12]:
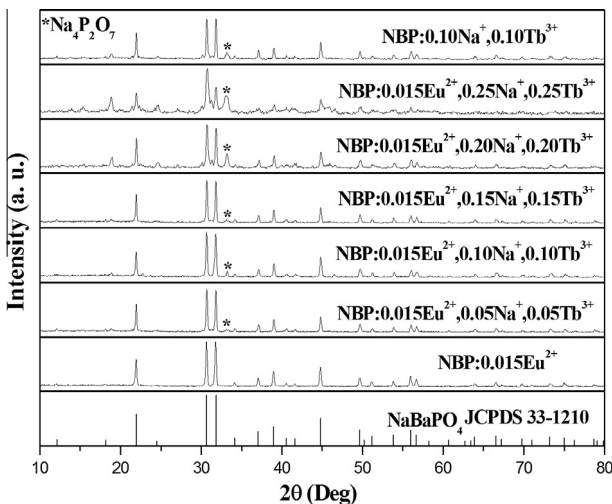
$$I = A_1 \exp(-t/\tau_2) + A_2 \exp(-t/\tau_2) \tag{1}$$

Fig. 1. XRD patterns of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25$) and NBP: $0.1Tb^{3+}$, $0.1Na^+$ phosphors.

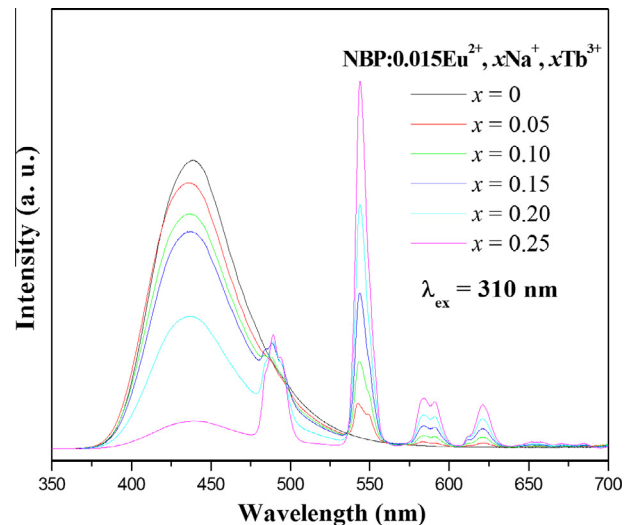**Fig. 3.** The emission spectra of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25$) phosphors ($\lambda_{ex} = 310$ nm).

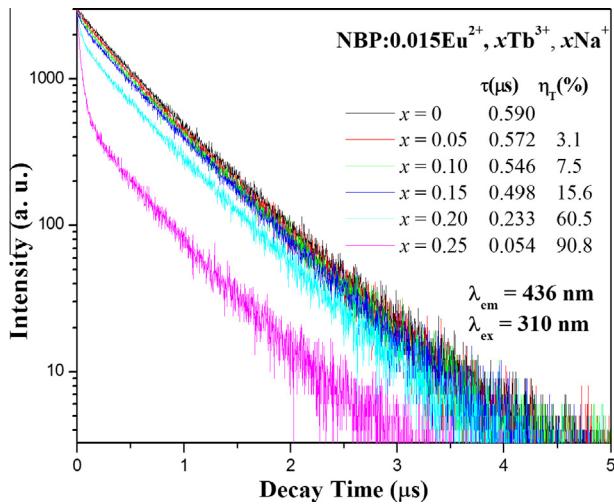**Fig. 4.** The decay curves of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ ($x = 0$, 0.05, 0.10, 0.15, 0.20, 0.25) phosphors ($\lambda_{em} = 436$ nm, $\lambda_{ex} = 310$ nm).

Fig. 5. The CIE chromaticity coordinate diagram of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ ($x = 0$, 0.05, 0.10, 0.15, 0.20, 0.25) and NBP: $0.1Tb^{3+}$, $0.1Na^+$ phosphors.

where I is the luminescence intensity, A_1 and A_2 are constants, t is the time and τ_1, τ_2 are the decay times for the exponential components. According to these parameters, the average decay times (τ) of Eu^{2+} ion can be calculated by the following equation [12]:

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \qquad (2)$$

The average decay times (τ) of Eu^{2+} ion are calculated to be 0.590, 0.572, 0.546, 0.498, 0.233 and 0.054 μs, respectively. In the Eu^{2+}, Tb^{3+} co-doped samples, if there is no energy transfer between Eu^{2+} and Tb^{3+}, or the energy transfer between Eu^{2+} and Tb^{3+} is a radiative energy transfer, the decay time of Eu^{2+} will be the same as in the Eu^{2+} singly doped sample. While if the energy transfer between Eu^{2+} and Tb^{3+} is a non radiative energy transfer, the decay time of Eu^{2+} will be shortened. As mentioned above, the decay times of Eu^{2+} in $NaBaPO_4$:$0.015Eu^{2+}$, xTb^{3+}, xNa^+($x = 0$, 0.05, 0.10, 0.15, 0.20, 0.25) phosphors get shorter with the increasing Tb^{3+} concentration, which confirmed the resonance type energy transfer between the Eu^{2+} and Tb^{3+} ions in $NaBaPO_4$ host. The energy difference between the lowest 5d excited level ($\sim$28,818 cm^{-1}) of Eu^{2+} ion and the excited $^5D_3$ level ($\sim$26,525 cm^{-1}) of Tb^{3+} is about 2293 cm^{-1}, which is close to twice the highest vibration energy ($\nu_{max} \approx 1037$ cm^{-1}) in phosphate [13]. Therefore, it is expected that the energy transfer occurs via non radiative transitions from the lowest 5d level of Eu^{2+} to the $^5D_3$ level of Tb^{3+} ion by assistance of two phonons.

The energy transfer efficiency (η_T) from Eu^{2+} to Tb^{3+} can be expressed by [12]:

$$\eta_T = 1 - \tau_S/\tau_{S0} \qquad (3)$$

where τ_{S0} and τ_S are the lifetimes of the Eu^{2+} in the absence and the presence of the Tb^{3+}, respectively. The η_T was determined to be 3.1%, 7.5%, 15.6%, 60.5% and 90.8% for NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ phosphors with $x = 0.05$, 0.10, 0.15, 0.20 and 0.25, respectively. As shown in the inset of Fig. 4, the η_T is found to increase gradually with increasing Tb^{3+} content.

The CIE chromaticity coordinates of NBP: $0.015Eu^{2+}$, xTb^{3+}, xNa^+ and NBP: $0.1Tb^{3+}$, $0.1Na^+$ phosphors are shown in Fig. 5. With increasing Tb^{3+} concentration, the ratio of emission intensity between Eu^{2+} and Tb^{3+} changes. The CIE coordinates of the phosphors change from (0.154, 0.064) to (0.287, 0.452) for $x = 0$ and 0.25, respectively. The hue of the phosphors varies from blue to green with increasing Tb^{3+} content. The CIE chromaticity coordination of NBP: $0.1Tb^{3+}$, $0.1Na^+$ phosphor is (0.281, 0.510), which locates
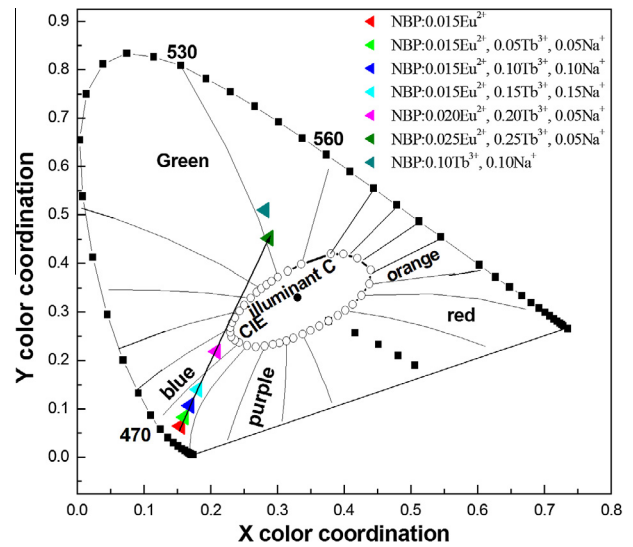
at the green spectra region. Therefore, a tunable blue to green light can be obtained by appropriately changing the ratio of Eu^{2+}/Tb^{3+}.

4. Conclusions

A series of NBP: Eu^{2+}, Tb^{3+}, Na^+ phosphors were prepared by solid state reaction. The NBP:Eu^{2+}, Tb^{3+}, Na^+ phosphors has both the broad band emission due to Eu^{2+} ion and the sharp green emission due to Tb^{3+} ion. The energy transfer from Eu^{2+} to Tb^{3+} in $NaBaPO_4$ host is demonstrated to be an effective resonance non-radiative energy transfer. The relative intensity ratio of blue and green emission could be tuned by adjusting the contents of Eu^{2+} and Tb^{3+} in NBP: Eu^{2+}, Tb^{3+}, Na^+. Due to the strong absorption ranging from 250 to 400 nm in the excitation spectrum of NBP: Eu^{2+}, Tb^{3+}, Na^+ phosphor, it is a potential phosphor applicable to n-UV chip for white LEDs.

Acknowledgments

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