The concentration quenching characteristics of $^5D_3$-$^7F_J$ and $^5D_4$-$^7F_J (J=0—6)$ transitions of Tb$^{3+}$ in YBO$_3$:Tb$^{3+}$ phosphor

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The photoluminescence quenching behaviors of $^5D_3$-$^7F_J$ and $^5D_4$-$^7F_J (J=0—6)$ transitions of Tb$^{3+}$ in YBO$_3$:Tb under 130—290 nm excitation were systematically investigated. The results revealed that the quenching concentrations of both $^5D_3$-$^7F_J$ and $^5D_4$-$^7F_J$ transitions of Tb$^{3+}$ in YBO$_3$:Tb were mainly dependent on excitation wavelength. Particularly, the quenching concentrations of $^5D_4$-$^7F_J$ transitions of Tb$^{3+}$ under 130—290 nm excitation were correlated with excitation bands of YBO$_3$:Tb. The quenching concentrations of $^5D_3$-$^7F_J$ transitions remained at low concentration (2%) under 186—290 nm excitation and then increased gradually with energy of incoming excitation photon when excited at 130—186 nm. This dependence should be involved in their excitation mechanisms and quenching pathway in particular excitation region.

The emission intensity of many phosphors as a function of activator concentration initially increases with activator concentration and then decreases, going through a maximum at some concentration. The decreases in emission intensity at a certain activator concentration are referred to as the phenomenon of “concentration quenching”[1,2]. And the optimal activator concentration with the highest emission intensity is considered as “quenching concentration” of phosphors. A complete characterization of the emission quenching behaviors in inorganic phosphors is very important not only for technological design but also for the basic understanding of the physical excitation processes[3—7].

On the other hand, YBO$_3$:Tb with high absorption edge and short decay time in vacuum ultraviolet (VUV) region is an inorganic green phosphor used in plasma display panels (PDPs), Hg-free lamps and back lighting fields[8,9]. Generally, the emission of Tb$^{3+}$ consists of the $^5D_3$-$^7F_J$ and $^5D_4$-$^7F_J (J=0—6)$ transitions. Among them, the $^5D_4$-$^7F_5$ transition at 543 nm is the dominant emission and mainly contributes to the green component. The presence of $^5D_3$-$^7F_J$ transitions at 380—480 nm not only decreases the emission intensity of $^5D_4$-$^7F_5$ transition but also leads to chromaticity problems[10]. Therefore, a fundamental study on the emission and quenching characteristics of $^5D_3$-$^7F_J$ transitions is as important as that on the $^5D_4$-$^7F_5$ transition for YBO$_3$:Tb phosphors.

In recent years, much attention has been paid to the emission characteristics of $^5D_4$-$^7F_5$ transition of Tb$^{3+}$-doped phosphors[8—12]. However, there are few reports about the fundamental study on quenching behaviors of both $^5D_3$-$^7F_J$ and $^5D_4$-$^7F_J$ transitions of Tb$^{3+}$-doped phosphors in VUV region.

In this work, the emission characteristics of the $^5D_{3,4}$-$^7F_J (J=0—6)$ transitions of YBO$_3$:Tb phosphors under
130—290 nm excitation were investigated and compared systematically. And a possible energy relaxation mechanism of $^5D_{3,4} \rightarrow ^7F_J (J=0-6)$ transitions of YBO$_3$:Tb in VUV region was proposed.

1 Experimental

The Tb$_2$O$_3$ and Y$_2$O$_3$ (99.99%) were used as the starting materials and H$_3$BO$_3$ provided the boron source. The YBO$_3$:Tb samples were prepared by the conventional solid-state method in platinum crucible first at 500 °C for 3 h and then at 1100 °C for 3 h in air.

All the products were characterized as single phase by Rigaku D/max-2000 powder X-ray diffraction using CuKα ($\lambda$=1.5418 Å) radiation. Their photoluminescence excited with 130—290 nm was recorded on a FLS-920T (130—200 nm) and ARC model VM-504 vacuum monochromator (200—290 nm). All the spectra were recorded at room temperature.

2 Results and discussion

Figure 1 shows the emission spectra of Y$_{1-x}$BO$_3$:Tb$_x$ samples excited at 254 nm. The main emission peaks are located at about 487, 543, 585 and 624 nm as transitions from $^5D_4$ to $^7F_{5,6,7,8}$, respectively. Among them, the green $^5D_4 \rightarrow ^7F_5$ emission at 543 nm is dominant and its quenching concentration is about 12%. As far as the $^5D_3 \rightarrow ^7F_J$ transitions are concerned, the weaker emissions at about 385 and 470 nm which are due to the fact that $^5D_3 \rightarrow ^7F_6$ and $^5D_3 \rightarrow ^7F_2$ transitions of Tb$^{3+}$ reach the maxima when Tb$^{3+}$ content is 2%. However, when the Tb$^{3+}$ content increases to 6%, the emissions of all $^5D_3 \rightarrow ^7F_J$ transitions are completely quenched by cross relaxation process, as described by Formula (1). This cross relaxation process produces rapid population of the $^5D_4$ level at the expense of $^5D_3$ level, resulting in a stronger emission from $^5D_4 \rightarrow ^7F_0$ level.

\[
\text{Tb}^{3+}(^5D_3) + \text{Tb}^{3+}(^7F_6) \rightarrow \text{Tb}^{3+}(^5D_4) + \text{Tb}^{3+}(^7F_0). \tag{1}
\]

Figure 2 shows the emission spectra of Y$_{1-x}$BO$_3$:Tb$_x$ samples under 147 nm excitation. The spectral features of $^5D_4 \rightarrow ^7F_J$ transitions of Tb$^{3+}$ in YBO$_3$:Tb are similar to those excited with 254 nm. However, the quenching concentration of $^5D_3 \rightarrow ^7F_5$ transition is shown to be 6%, much lower than that of 12% under 254 nm excitation. As for $^5D_3 \rightarrow ^7F_J$ transitions, the emissions at about 385 and 470 nm increase with Tb$^{3+}$ content and reach the maxima at Tb$^{3+}$ = 14%. And when the Tb$^{3+}$ content is increased to 18%, all the $^5D_3 \rightarrow ^7F_J$ transitions completely disappear for cross relaxation process.

From the above discussion, it can be concluded that the quenching concentrations of $^5D_3 \rightarrow ^7F_J$ transitions of Tb$^{3+}$ are very different from that of $^5D_4 \rightarrow ^7F_5$ transitions of Tb$^{3+}$ in YBO$_3$:Tb. However, this difference is understandable because the concentration quenching mechanisms of $^5D_4 \rightarrow ^7F_J$ and $^5D_3 \rightarrow ^7F_J$ transitions of Tb$^{3+}$ in YBO$_3$:Tb are completely different. In general, when Tb$^{3+}$ content reaches a critical value, the $^5D_4 \rightarrow ^7F_J$ transitions of Tb$^{3+}$ would be quenched for non-radioactive energy transfer process among Tb$^{3+}$ ions$^{[1,2]}$, while the concentration quenching effect of $^5D_3 \rightarrow ^7F_J$ transitions is due to cross relaxation process between Tb$^{3+}$-pairs$^{[10,11]}$.

Especially, it is important to note that the quenching concentrations of both $^5D_4 \rightarrow ^7F_J$ and $^5D_3 \rightarrow ^7F_J$ transitions of YBO$_3$:Tb excited with 147 nm (VUV) are different from...