The Photoluminescent Quenching Behaviors of Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ Phosphors

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**Abstract.** The quenching behaviours of $^5$D$_{4}$-$^7$F$_{6}$ emission of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ under 125-300nm excitation were systematically investigated. The results revealed that its luminescent quenching concentrations excited at particular wavelengths were dependent on corresponding excitation bands. On analyzing the luminescent quenching characteristics, all these spin-orbit 4f-5d transitions of Tb$^{3+}$ and host absorption band in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ were identified in excitation spectrum and the energy levels scheme of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ system was first established.

1. Introduction

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. Generally, more activators in host means more emission centers and higher luminescent intensity, thus the phosphors with high quenching concentration are expected. Moreover, 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, the Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ was reported as a recently developed green phosphor with high quenching concentration and excellent photoluminescence in ultraviolet region [8-11]. Developing a model to study quenching behaviors in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ was significant to understand its photoluminescence properties, excitation pathways and quenching mechanisms, even developing some novel phosphors with efficient photoluminescence.

It was our fundamental aim to clarify the quenching and excitation mechanism of Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{1+}$ phosphor. In this work, the characteristics of quenching concentration in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{1+}$ under 130-290nm were investigated and the relationship between quenching concentrations and excitation bands was revealed. Based on these results, the host absorption and complete 4f-5d transitions of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ were successfully identified and the energy levels scheme of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ was established.
2. Experimental
All the Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ samples were synthesized by solid state method. The starting materials were Na$_2$CO$_3$ (A.R.), H$_3$BO$_3$ (A.R.), La$_2$O$_3$ (99.99%) and Tb$_4$O$_7$ (99.99%). The stoichiometric amount of reactants was mixed and ground homogeneously with excess of 3% H$_3$BO$_3$ to compensate the evaporation. Then, the mixed powders were sintered at 500$^\circ$C for 10h. Cooled and reground, then heated at 1100$^\circ$C for 24h twice with the intermediate grindings to obtain the phosphors. The excitation and emission spectra were measured at room temperature using an Edinburgh Instruments FLS920T combined. The light source of the VUV excitation part of the spectrometer system was a 150W Deuterium lamp (Cathodeon Incorporated) and the emission and excitation spectra were measured by the vacuum monochromator (VM504, Acton Research Corporation, ARC). The VUV excitation spectra were corrected by dividing the excitation intensity of sodium salicylate at the same measurement conditions.

3. Results and discussion
3.1. Photoluminescence at 147nm and 254nm
The 147nm and 254nm was the most typical excitation sources for application in vacuum ultraviolet (VUV) and ultraviolet (UV) region, respectively. Fig.1 showed the emission spectra of typical Na$_3$La$_9$O$_3$(BO$_3$)$_8$:0.1Tb$^{3+}$ samples under 147nm and 254nm excitation as representative. As shown in Fig.1, the emission intensity of samples excited at 147nm was much higher than that at 254nm. The main emission peaks at about 476, 543, 570 and 621nm were due to the $^{5}$D$_{4}$-$^{7}$F$_{6}$, $^{5}$D$_{4}$-$^{7}$F$_{5}$, $^{5}$D$_{4}$-$^{7}$F$_{4}$ and $^{5}$D$_{4}$-$^{7}$F$_{3}$ transitions of Tb$^{3+}$ respectively \[12\] and the $^{5}$D$_{4}$-$^{7}$F$_{3}$ at 543nm was dominant.

![Figure 1. emission spectra of Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ under 147nm and 254nm excitation, respectively.](image)

![Figure 2. the quenching concentration curves of Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ samples excited at 147nm.](image)

3.2. Quenching characteristics and identification of excitation bands under 125-300nm
In order to clarify the relationship between quenching concentrations and excitation wavelengths, the quenching concentrations of Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ under 125-300nm were investigated systematically. Table I exhibited the quenching concentrations of $^{5}$D$_{4}$-$^{7}$F$_{5}$ transition of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ samples excited at 125-300nm and it was significant to find that: under 260-290nm excitation, the quenching concentration of Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ was about 14% which differed from the neighbor excitation regions. As shown in excitation spectrum of Na$_3$La$_9$O$_3$(BO$_3$)$_8$:Tb$^{3+}$ (Fig.3), this broad excitation band at 255-293nm was also observed and it could be ascribed to the lowest spin-forbidden
transition to $^5D_3$ term of Tb$^{3+}$ based on Ref [13-15]. When excited at 220-245nm, the quenching concentrations of Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ varied to 10%. The high

Table 1. the quenching concentrations of $^5D_4$-$^7F_5$ transition of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ samples when excited by 125-300nm.

| Excitation wavelength/nm | Quenching concentrations | Excitation bands | Host absorption | Spin-allowed transitions to $^7D_5$ term of Tb$^{3+}$ |
|--------------------------|--------------------------|------------------|-----------------|----------------------------------------------|
| 125                      | 26%                      | 16%              | 16%             | 16%                                          |
| 130                      | 24%                      | 16%              | 16%             | 16%                                          |
| 134                      | 16%                      | 16%              | 16%             | 16%                                          |
| 138                      | 16%                      | 16%              | 16%             | 16%                                          |
| 142                      | 16%                      | 16%              | 16%             | 16%                                          |
| 146                      | 16%                      | 16%              | 16%             | 16%                                          |
| 148                      | 16%                      | 16%              | 16%             | 16%                                          |

excitation peak at around 217-246nm could also be observed in excitation spectrum in Fig.3 and it has been attributed to the lowest spin-allowed transition to $^7D_5$ term of Tb$^{3+}$ [13-15]. In addition, these results indicated that the quenching concentration of spin-allowed transition was less than that of spin-forbidden transition. According to Ref [1,16], More energetic photons induced electronic transitions from the 4f$^8$ ground state toward $d$-states belonging to the first excited configuration 4f$^{n-1}5d$. These electric dipole transitions occurred between two configurations of opposite parity and were allowed at first-order. Consequently, the 4f-5d transitions were in general sensitive to rare earth concentration resulting in less quenching concentration when they were spin allowed.

Figure 3. the comparison of excitation spectra of Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ and Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Eu$^{3+}$ monitored at 543nm and 611nm, respectively.

Figure 4. the identification of excitation spectrum of Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ sample monitored at 543nm.
As far as the excitation region in 125-215nm was concerned, it mainly consisted of host absorption band and higher spin-orbit 4f-5d transitions of Tb$^{3+}$ which were seldom identified because of the bands overlaps. In order to understand the fundamental excitation mechanism for Na$_{3}$La$_{9}$O$_{3}$(BO$_{3}$)$_{8}$:Tb$^{3+}$, all these excitation bands should be identified. In particular, the quenching concentrations gave some useful information on these identifications. As shown in Table I, in the interval of 130-158nm, the quenching concentrations were 16% and it could be attributed to the borate host absorption band [17,18]. On the other hand, both the excitation spectra of Na$_{3}$La$_{9}$O$_{3}$(BO$_{3}$)$_{8}$:Tb$^{3+}$/Eu$^{3+}$ (Fig.3) showed the strong absorption band centered at 146nm and this result confirmed our above attribution of host absorption. In addition, the region of 206-215nm could be ascribed to the spin-forbidden transitions to $^9$D$_{4}$ term of Tb$^{3+}$ (denoted as “B” in Fig.4) because of its larger quenching concentrations while the region of 160-204nm belonged to the spin-allowed $^7$F$_{6}$-$^7$D$_{J}$ ($J=4,3,2,1$) transitions of Tb$^{3+}$.

**Figure 4.** the identification of excitation spectrum of Na$_{3}$La$_{9}$O$_{3}$(BO$_{3}$)$_{8}$:Tb$^{3+}$ monitored at 543nm. Based on the above results, the excitation peak centered at 161nm near host absorption in Fig.4 could be assigned to the higher spin-orbit 4f-5d transition of Tb$^{3+}$. In general, the energy gap between the lowest and the highest 4f-5d transitions of Tb$^{3+}$ was about 18000 cm$^{-1}$ [11]. Therefore, the highest spin allowed 4f-5d transition was theoretically expected to be located at around 61290 (43290+18000) cm$^{-1}$ (163nm). In fact, a strong excitation peak at around 62112 cm$^{-1}$ (161nm) was observed in the excitation spectrum (Fig.4) and so this peak could be attributed to the highest spin allowed 4f-5d transition ($^7$F$_{5}$-$^7$D$_{1}$, denoted as “e”). Consequently, the energy gap between the lowest and the highest 4f-5d levels of Tb$^{3+}$ in Na$_{3}$La$_{9}$O$_{3}$(BO$_{3}$)$_{8}$:Tb$^{3+}$ was calculated to be about 18822 (62112-43290) cm$^{-1}$ which was obviously larger than that of most Tb$^{3+}$ doped inorganic phosphors [11].

According to the obtained energy gap of Na$_{3}$La$_{9}$O$_{3}$(BO$_{3}$)$_{8}$:Tb$^{3+}$ system, the energy of the highest spin forbidden 4f-5d transition ($^7$F$_{6}$-$^7$D$_{4}$, “E”) could also be calculated to be at about 54924 (36102+18822) cm$^{-1}$. Considering that the energy of small excitation shoulder at 57143 cm$^{-1}$ was higher than that of the highest spin forbidden 4f-5d transition (54923 cm$^{-1}$, “E”), it could be attributed to be the second highest spin allowed 4f-5d transition (denoted as “d”) of Tb$^{3+}$. And the broad excitation peaks at around 54645 cm$^{-1}$ and 51813 cm$^{-1}$ should be ascribed to the spin allowed $^7$F$_{5}$-$^7$D$_{3}$ and $^7$F$_{6}$-$^7$D$_{4}$ transition (denoted as “c” and “b”) which overlaps part of the highest spin-forbidden $^7$F$_{5}$-$^7$D$_{4}$ (“E”).

By comparing the same yardstick of five crystal field split levels of the d-electron in Fig.4, these weaker excitation peaks at about 45455, 47846 and 50761 cm$^{-1}$ should belong to the spin forbidden $^7$F$_{6}$-$^7$D$_{4}$ (denoted as “B”), $^7$F$_{6}$-$^7$D$_{3}$ (“C”) and $^7$F$_{5}$-$^7$D$_{3}$ (“D”) transitions, respectively and the results was similar to the calculation on the 5d energy level positions of Tb$^{3+}$ in some other inorganic compounds by P.Dorenbos [12].
Basing on the above experimental crystal field split energies, the complete energy levels scheme of Tb$^{3+}$ for Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ system was first illustrated in Fig.5. Using this scheme, some suitable luminescence sensitizer matching the energy levels of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ system can be selected.

![Energy level scheme of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$](image)

**Figure 5.** The energy level scheme of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ samples. The levels are anticipated based on the results of this work.

### 4. Conclusions

It was revealed that the photoluminescent quenching concentrations of Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ at particular excitation wavelengths were dependent on excitation bands in essence. By studying the quenching behaviors, these characteristic spin-orbit 4$f$-5$d$ transitions of Tb$^{3+}$ and host absorption band in Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ were completely identified and the energy levels scheme of Tb$^{3+}$ in Na$_3$La$_9$O$_3$(BO$_3$)$_6$:Tb$^{3+}$ was first established.

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