Luminescent property and energy transfer from Ce^{3+} to Tb^{3+} in YAl$_3$(BO$_3$)$_4$*

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A series of Ce^{3+}, Tb^{3+} or Ce^{3+}/Tb^{3+} doped YAl$_3$(BO$_3$)$_4$ phosphors are synthesized by a high temperature solid-state reaction, and their luminescent properties are investigated. YAl$_3$(BO$_3$)$_4$:Ce^{3+} shows a broad emission band at 422 nm under the 367 nm radiation excitation. YAl$_3$(BO$_3$)$_4$:Tb^{3+} can be efficiently excited by the ultraviolet (UV) light, and produces green emission. The emission intensity of YAl$_3$(BO$_3$)$_4$:Tb^{3+} can be enhanced by adjusting Tb^{3+} doped content, and reaches the maximum at 0.06 mol Tb^{3+}. When Ce^{3+} is codoped, the emission intensity of Tb^{3+} in YAl$_3$(BO$_3$)$_4$ can be enhanced, but the commission international del'eclairage (CIE) chromaticity coordinates of YAl$_3$(BO$_3$)$_4$:Tb^{3+} have almost no change. Moreover, the energy transfer from Ce^{3+} to Tb^{3+} in YAl$_3$(BO$_3$)$_4$ is studied.

White light-emitting-diodes (LEDs) have been paid much attention as the next-generation solid state lighting due to their superior features, such as the low power consumption, high efficiency, environment-friendliness, long persistence, and applicability in final products in a wide range of sizes[1-3]. Currently, the most common and simple method is combining a blue LED chip with a yellow light emitting phosphor YAG:Ce, which emits the greenish-yellow light, but it is deficient in the red spectral region, which leads to the white LEDs with a poor color rendering property[4]. Therefore, the other methods to achieve white LED are suggested. For example, the white LED can be obtained by combining the tri-color (red, green and blue) phosphor or a single-phase white emitting phosphor with an ultraviolet (UV) or near-ultraviolet (n-UV) LED. The white LED has better spectral characteristics and color rendering property. Therefore, for increasing the efficiency of white LEDs, more and more attention has been paid to the development of the new tri-color or white light emitting phosphor which can be excited in the range of UV or n-UV light[5-7]. Generally, the broad band emitter is usually used to sensitize the luminescence of rare earth and transition metal ions. Specially, Ce^{3+} ion shows efficient broad band emission due to its 5d-4f electric dipole allowed transitions[8]. Ce^{3+} ion acts as a good sensitizer in co-doped materials, and transfers a part of its energy to the activator ions, such as Eu^{2+}, Tb^{3+} and Mn^{2+}[9-11]. Generally, the kind of energy transfer belongs to resonance type. In recent years, the resonance energy transfer between the impurity ions in the luminescent material becomes an intense research subject, mainly because of its importance in the development of efficient phosphor materials for solid state lighting.

As an important family of luminescent materials, borate has attracted much attention, such as rare-earth ions doped YAl$_3$(BO$_3$)$_4$[12-14]. However, to the best of our knowledge, little attention has been paid to the luminescent property of Ce^{3+}/Tb^{3+} co-doped YAl$_3$(BO$_3$)$_4$. Among the rare-earth ions, Ce^{3+} and Tb^{3+} ions are two of the most important luminescent centers. Therefore, in this paper, the luminescent property and the energy transfer from Ce^{3+} to Tb^{3+} in YAl$_3$(BO$_3$)$_4$ are investigated, and it may be a suitable green emitting phosphor for white LEDs.

The samples were synthesized by the high temperature solid-state reaction technique. According to the molecular formula of Y$_{1-x-y}$Al$_3$(BO$_3$)$_4$:xCe^{3+}, yTb^{3+}, the raw materials of Y$_2$O$_3$, Al$_2$O$_3$, H$_3$BO$_3$, CeO$_2$ and Tb$_4$O$_7$, which are all of analytical grade, were stoichiometrically weighed and thoroughly mixed in an agate mortar. The mixed powder was calcined in corundum crucibles at 1300 ℃ for 4 h in air. Finally, the samples were cooled down to room temperature and ground thoroughly again into powder. Moreover, all the samples were sieved under the same condition to ensure the similar particle size distribution.

The final phase was checked with a conventional X-ray diffraction (XRD) (D/max-rA, CuKα, 40 kV, 100 mA, λ=0.15406 nm). The spectral characteristics of the phosphors were performed by using a Hitachi F-4600 fluorescence spectrophotometer equipped with a 450 W Xe lamp. The commission international de l'eclairage (CIE) chromaticity coordinates were measured by a PMS-80 UV-VIS-NEAR IR spectrorphotocolorimeter. The measurements were performed at room temperature.

The XRD patterns of $YAl_3(BO_3)_4$: xCe^{3+}, yTb^{3+} were measured, and the similar diffraction patterns were observed for each sample. It means that doping a little Ce^{3+}, Tb^{3+} or Ce^{3+}/Tb^{3+} has no influence on the crystal structure of $YAl_3(BO_3)_4$. As a representation, the results of $YAl_3(BO_3)_4$:$0.005Ce^{3+}$, $0.06Tb^{3+}$ are shown in Fig.1. There is no obvious difference between the experimental data and the standard joint committee of powder diffraction standard (JCPDS) card (No.15-0117). $YAl_3(BO_3)_4$ has a hexagon crystal structure with a space group of R-32 (155), and the lattice parameters are $a=b$=0.9293 nm and c=0.7245 nm.
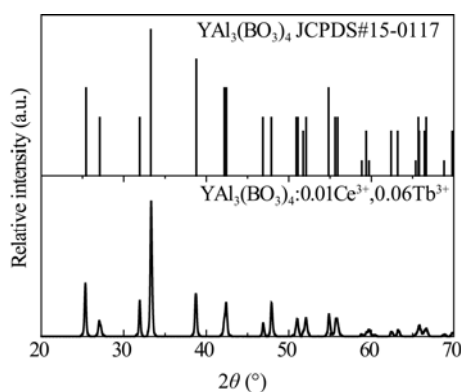
**Fig.1 XRD pattern of $YAl_3(BO_3)_4$:$0.005Ce^{3+}$, $0.06Tb^{3+}$ with the standard data of $YAl_3(BO_3)_4$ (JCPDS No.15-0117)**

Fig.2 presents the excitation and emission spectra of Ce^{3+}, Tb^{3+} and Ce^{3+}/Tb^{3+} in $YAl_3(BO_3)_4$. Fig.2(a) shows $YAl_3(BO_3)_4$:$0.005Ce^{3+}$ has an asymmetric band extending from 360 nm to 500 nm with a maximum at 422 nm under the 367 nm radiation excitation. Monitored at 422 nm, the excitation spectrum of $YAl_3(BO_3)_4$:$0.005Ce^{3+}$ has a broad band in the region of 200−400 nm, due to the 4f-5d transition of Ce^{3+} ions, and the excitation peak is at 367 nm.

As shown in Fig.2(b), $YAl_3(BO_3)_4$:$0.06Tb^{3+}$ has many emission lines which correspond to the transitions from the $^5D_4$ excited state to the ^7F_J ground states of Tb^{3+}, such as $^5D_4\rightarrow^7F_6$ (481 nm), $^5D_4\rightarrow^7F_5$ (544 nm), $^5D_4\rightarrow^7F_4$ (587 nm) and $^5D_4\rightarrow^7F_3$ (639 nm). The intensity of $^5D_4\rightarrow^7F_5$ transition is much higher than that of the other transitions, resuting in a dominant green emission. Monitored at 544 nm emission, $YAl_3(BO_3)_4$:$0.06Tb^{3+}$ has an excitation band at 241 nm which is attributed to the $4f^8$-$4f^75d^1$ transition of Tb^{3+}, and the 356 nm and 376 nm excitation peaks are

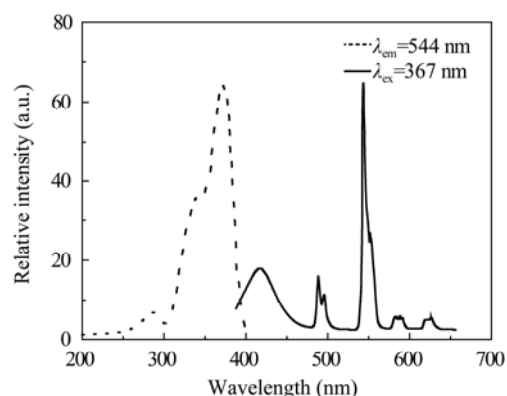due to the f-f transition taking place from the ground $^7F_6$ level.
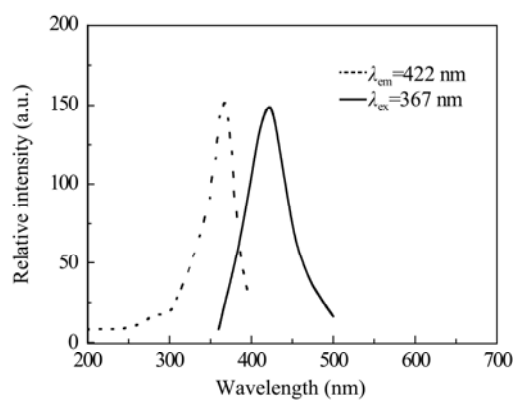
(a) $YAl_3(BO_3)_4$:$0.005Ce^{3+}$
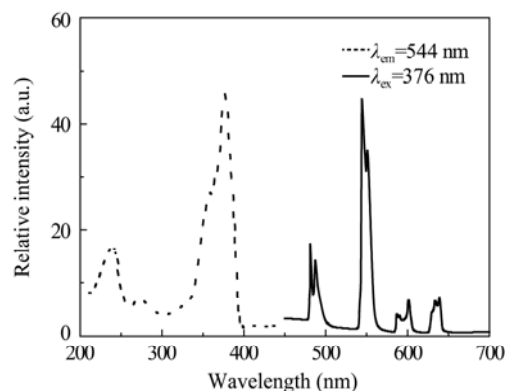
(b) $YAl_3(BO_3)_4$:$0.06Tb^{3+}$

(c) $YAl_3(BO_3)_4$:$0.005Ce^{3+}$, $0.06Tb^{3+}$

Fig.2 Excitation and emission spectra of samples

Fig.2(c) shows that $YAl_3(BO_3)_4$:$0.005Ce^{3+}$, $0.06Tb^{3+}$ has not only an obvious blue band from Ce^{3+} but also a strong green line from Tb^{3+} under the 367 nm radiation excitation. Monitored at the 544 nm emission of Tb^{3+}, the excitation spectrum shows a broad band, which is different from that of only Tb^{3+} doped $YAl_3(BO_3)_4$, and it contains significant additional contribution from Ce^{3+}. It may mean that the energy transfer from Ce^{3+} to Tb^{3+} occurs. When comparing the emission spectrum of $YAl_3(BO_3)_4$:Ce^{3+} with that of $YAl_3(BO_3)_4$:Tb^{3+}, the result shows a small spectral over-

lap. However, the overlap is very small in the case of $YAl_3(BO_3)_4:Ce^{3+}$, Tb^{3+}, which means the energy transfer efficiency of the resonant radiative transfer is very low. And the similar results have been discussed extensively[15,16]. Therefore, the exchange interaction energy transfer behavior may occur accompanied with the resonant energy transfer.

Fig.3 depicts the emission spectra of $YAl_3(BO_3)_4:xCe^{3+}$, $0.06Tb^{3+}$ with different Ce^{3+} doping contents. Under the 367 nm radiation excitation, an obvious blue emission of Ce^{3+} and a green emission peak are observed in the emission spectra of all samples. And the emission intensities of Tb^{3+} and Ce^{3+} are obviously increased with increasing the Ce^{3+} doped content from 0.005 mol to 0.03 mol. The inset of Fig.3 presents that the green emission intensity of Tb^{3+} in the Ce^{3+} co-doped phosphor (I_s) is stronger than that of Tb^{3+} singly doped phosphor (I_{so}), which is attributed to the energy transfer from Ce^{3+} to Tb^{3+}. And it is obviously observed that the emission intensity of Tb^{3+} (I_s) gradually increases with increasing the Ce^{3+} doped content, because Ce^{3+} transfers more and more energy to Tb^{3+}.
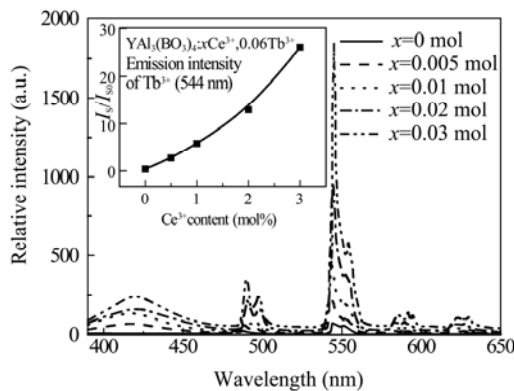
Fig.3 Emission spectra of YAl₃(BO₃)₄:xCe³⁺, 0.06Tb³⁺ with different Ce³⁺ doping contents (The inset is the emission intensity of Tb³⁺ as a function of Ce³⁺ doped content.)

In order to prove the energy transfer from Ce^{3+} to Tb^{3+}, the emission intensities of Ce^{3+} in $YAl_3(BO_3)_4$ with and without Tb^{3+} are measured, and as shown in Fig.4. The results show that the emission intensity of Ce^{3+} singly doped phosphor is obviously higher than that of co-doped Tb^{3+} phosphor, and it means that a part of energy is transferred to Tb^{3+}.

For $YAl_3(BO_3)_4:Ce^{3+}$, Tb^{3+}, the energy transfer plays an important role. The 5d-4f transition of Ce^{3+} is electric-dipole allowed, which is stronger than the forbidden 4f-4f electronic transitions within $4f^n$ configurations of Tb^{3+}. Therefore, Ce^{3+} can strongly absorb ultraviolet (UV) radiation and efficiently transfer its energy to Tb^{3+} to enhance the emission of Tb^{3+}. The Ce^{3+} ions act as sensitizer and the Tb^{3+} ions act as activators in the system.
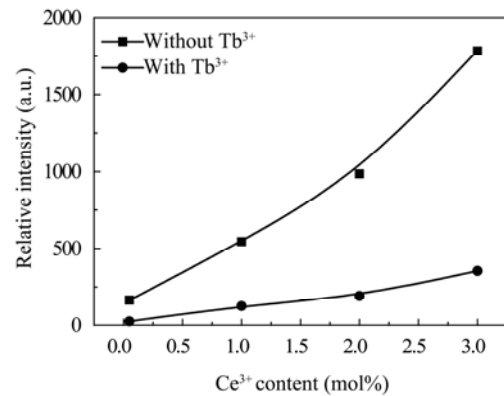
Fig.4 Emission intensities of Ce³⁺ in YAl₃(BO₃)₄ with and without Tb³⁺

Fig.5 shows the schematic diagram of energy level with the electronic transitions (Ce^{3+}, Tb^{3+}) and the energy transfer process ($Ce^{3+} \to Tb^{3+}$). The optical properties of $YAl_3(BO_3)_4:Ce^{3+}$, Tb^{3+} are determined by the transitions between f-electron and d-electron states of cerium and between different f-electron states of terbium. Upon UV radiation excitation, the energy transfer takes place from 5d (Ce^{3+}) to the high excitation levels of Tb^{3+} ($4f^n$) followed by the cross relaxation to the $^5D_4$ level of Tb^{3+}, which decays to the lower levels of ^7F_J (J= 6, 5, 4, 3)[17].
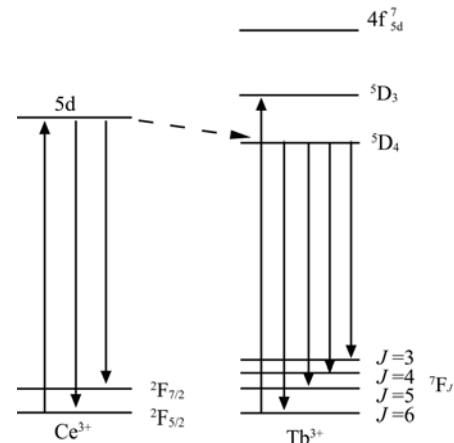
Fig.5 Schematic diagram of energy level in YAl₃(BO₃)₄: Ce³⁺, Tb³⁺ with electronic transitions and energy transfer processes

The CIE chromaticity coordinates of $YAl_3(BO_3)_4:xCe^{3+}$, $0.06Tb^{3+}$ are measured and shown in Tab.1. The results show that the CIE chromaticity coordinates of $YAl_3(BO_3)_4:xCe^{3+}$, $0.06Tb^{3+}$ are very close to those of $YAl_3(BO_3)_4:0.06Tb^{3+}$. That is to say, the co-doped Ce^{3+}, which can strengthen the emission intensity of Tb^{3+}, has almost no influence on the emission color. So it may be a suitable green phosphor for UV-based white LEDs.

Generally, the emission intensity of rare earth ions in compound is influenced by its doped content. For $YAl_3(BO_3)_4:Tb^{3+}$, its emission intensity is influenced by

Tab.1 CIE chromaticity coordinates of YAl$_3$(BO$_3$)$_4$:xCe^{3+}, 0.06Tb^{3+}

YAl$_3$(BO$_3$)$_4$:xCe^{3+}, 0.06Tb^{3+}	x=0	x=0.005	x=0.01	x=0.02	x=0.03
CIE (x, y)	(0.331, 0.579)	(0.331, 0.578)	(0.330, 0.578)	(0.329, 0.578)	(0.329, 0.578)

the Tb^{3+} doped content. As shown in the inset of Fig.6, with doping 0.06 mol Tb^{3+}, the concentration quenching of Tb^{3+} in YAl$_3$(BO$_3$)$_4$ occurs. Non-radiative energy transfer from one Tb^{3+} ion to another Tb^{3+} ion may occur by exchange interaction, radiation reabsorption or multiple-multiple interaction, and Tb^{3+} is an isolated emission center in YAl$_3$(BO$_3$)$_4$:Tb^{3+}. The transition of Tb^{3+} is allowed, while exchange interaction is responsible for the energy of forbidden transitions, and the typical critical distance is about 0.5 nm[18]. It means the mechanism of exchange interaction plays no role in the energy transfer between Eu^{3+} ions in YAl$_3$(BO$_3$)$_4$:Tb^{3+}. The mechanism of radiation reabsorption comes into effect only when there is a broad overlap between the fluorescent spectra of the sensitizer and activator, and the emission and excitation spectra of YAl$_3$(BO$_3$)$_4$:Tb^{3+} are unlikely to be observed in the case. The fluorescent mechanism of Tb^{3+} in YAl$_3$(BO$_3$)$_4$:Tb^{3+} is the electric multiple-multiple interaction by Dexter's theory. If the energy transfer occurs between the same sorts of activators, the intensity of
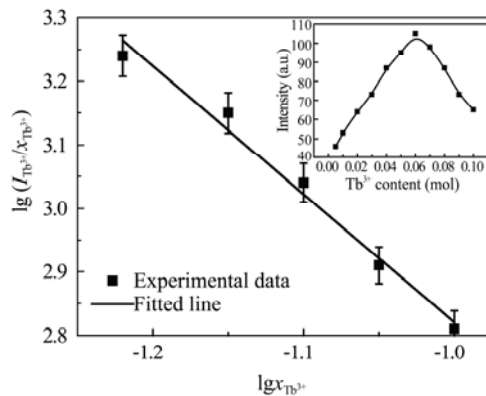
Fig.6 lg(I/ $x_{Tb^{3+}}$) as a function of lg $x_{Tb^{3+}}$ in YAl$_3$(BO$_3$)$_4$: Tb^{3+} phosphors (λ_{ex}=376 nm)

multipolar interaction can be determined. The emission intensity per activator ion follows the equation[19, 20] as

$$(I/x) = K\,[1+\beta\,(x)^{Q/3}]^{-1}, \tag{1}$$

where x is the activator concentration, Q=6, 8, 10 for dipole-dipole (d-d), dipole-quadrupole (d-p), quadrupole-quadrupole (q-q) interactions, respectively, and K and β are constants for the same excitation conditions for a given

host crystal.

Ce^{3+}, Tb^{3+} and Ce^{3+}/Tb^{3+} YAl$_3$(BO$_3$)$_4$ phosphors are synthesized by a high temperature solid-state method. Y$_{0.94}$Al$_3$(BO$_3$)$_4$:Ce^{3+} and Y$_{0.94}$Al$_3$(BO$_3$)$_4$:Tb^{3+} can be effectively excited by the UV light, and produce the blue and green emission, respectively. With co-doped Ce^{3+}, the emission intensity of Tb^{3+} in Y$_{0.94}$Al$_3$(BO$_3$)$_4$ can be obviously enhanced by the energy transfer from Ce^{3+} to Tb^{3+}, but its emission color can not be influenced. The results show that YAl$_3$(BO$_3$)$_4$:xCe^{3+}, 0.06Tb^{3+} may be a promising green emitting phosphor for UV-based white LEDs.

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