

Luminescence of $\text{YAl}_3(\text{BO}_3)_4$: Eu^{2+} , Dy^{3+} phosphor and its luminescence decay characteristics

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Abstract Eu^{2+} , Dy^{3+} co-doped $\text{YAl}_3(\text{BO}_3)_4$ phosphors are synthesized by sol-gel method. The phosphors show prominent blue luminescence due to the $4f^7-4f^65d$ transition of Eu^{2+} . The emission intensity is greatly improved when Dy^{3+} is doped into the $\text{YAl}_3(\text{BO}_3)_4$: Eu^{2+} system. The 1% Dy^{3+} in Eu^{2+} , Dy^{3+} co-doped $\text{YAl}_3(\text{BO}_3)_4$ phosphors is the optimum doping concentration. The luminescence decay characteristics of the samples have also been investigated, exhibiting the decay times of approximately 0.1 μs , which is much shorter compare to other Eu^{2+} doped phosphors.

Keywords phosphor · $\text{YAl}_3(\text{BO}_3)_4$ · Eu^{2+} · Dy^{3+} · Luminescence

1 Introduction

Eu^{2+} doped phosphors usually show strong broad band emission with a short decay time, so they have been widely

investigated in recent years [1–10]. The wavelength positions of the emission bands depend very much on the hosts, changing from the near-UV to the red. Eu^{2+} emission results from $4f^65d-4f^7(^8S_{7/2})$. As the position of the band corresponding to $4f^65d$ configuration is strongly influenced by the host, the emission can be located anywhere between 365 nm and 650 nm. Since the $4f-5d$ transition is an allowed dipole transition, the absorption and emission of Eu^{2+} is very efficient in many hosts, which makes the Eu^{2+} doped phosphors of practical importance.

When the crystal field is strengthened, the emission bands will shift to longer wavelengths. The luminescence peak energy of the $5d-4f$ transitions of Eu^{2+} are affected mostly by crystal parameters, specifically electron-electron repulsion.

In recent years, Eu^{2+} and Dy^{3+} co-doped phosphors are widely investigated, for example SrAl_2O_4 : Eu , Dy [11], $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$: Eu , Dy [12], $\text{SrAl}_{2-x}\text{B}_x\text{O}_4$: Eu^{2+} , Dy^{3+} nanocrystals [13], Eu^{2+} , Dy^{3+} co-doped $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Ca}_2\text{MgSi}_2\text{O}_7$ [14] etc. They are long-persistence phosphors and their luminescent results from the interaction between Eu^{2+} and Dy^{3+} . In this paper, the $\text{YAl}_3(\text{BO}_3)_4$: Eu^{2+} , Dy^{3+} phosphor samples with the rapid decay are prepared by using the sol-gel method, and the luminescence mechanism and other characteristics of the samples are measured and discussed.

2 Experimental

Y_2O_3 (99.9%), H_3BO_3 (>99.5%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>98.5%), Dy_2O_3 (99.9%) were used as starting materials. Stoichiometric amounts of the starting materials were dissolved in nitric acid (analytical purity). (The H_3BO_3 was 10% in excess). Then, the solution was evaporated to

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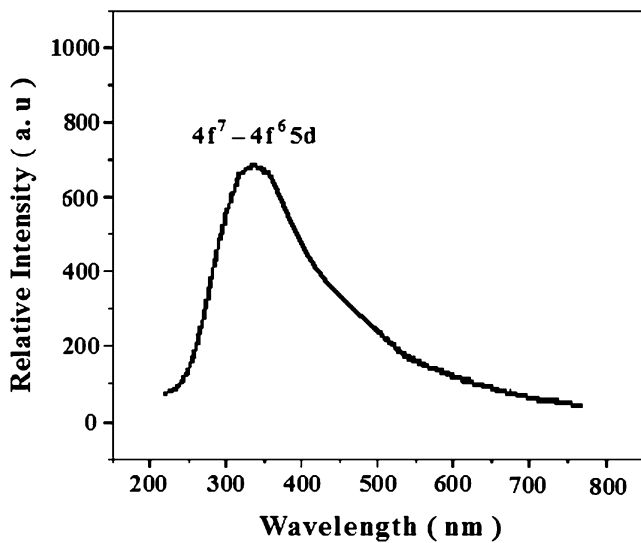


Fig. 1 The excitation spectrum of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_{0.03}^{2+}, \text{Dy}_{0.01}^{3+}$ annealed at 1100°C for 4 h. ($\lambda_{\text{em}}=420 \text{ nm}$)

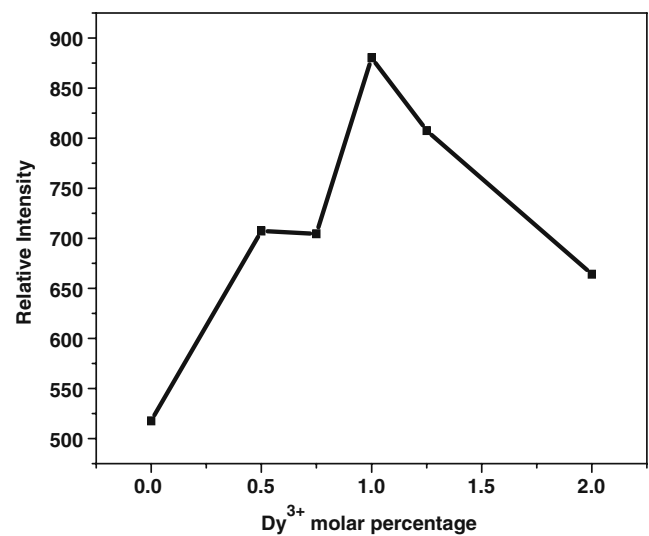


Fig. 3 Emission intensity of Dy^{3+} at 420 nm as a function of its doping concentration (x) in $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_{0.03}^{2+}, \text{Dy}_x^{3+}$ phosphors excited by 325 nm

dryness. The mixture was first pretreated at 723 K for one hour in air, and then ground powder. Subsequently, the powder was heated at 1327 K for four hours in a reducing atmosphere ($5\% \text{H}_2 + 95\% \text{N}_2$), then the products were let to cool down to room temperature. Finally, the products were ground to powder once more, and the target products were obtained.

The luminescence spectra of samples are measured using a JASCO FP-6500 spectro-fluorimeter equipped with a 450 W xenon lamp. Luminescence decay curves were obtained using a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) following a 300 nm laser excitation (Continuum Sunlite OPO, pulse width=4 ns). All the measurements were performed at room temperature.

3 Results and discussion

3.1 Luminescence properties

Figure 1 is the fluorescence excitation spectrum of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_x^{2+}, \text{Dy}_y^{3+}$, ($x=0.03, y=0.01$) measured at 420 nm. There is broad a mission band around 325 nm; it is the typical f-d transition of Eu^{2+} . Figure 2 shows the emission spectra of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_x^{2+}, \text{Dy}_y^{3+}$. There are two bands in the emission spectrum, the broad emission band at 430 nm is attributed to the $4f^6 5d(E_g) - 4f^7$ transition of Eu^{2+} , the band at 570 nm results from the $^4F_{9/2} - ^6H_{13/2}$ transition of Dy^{3+} . We can clearly observe that the emission intensity of the samples improved a lot compared with the

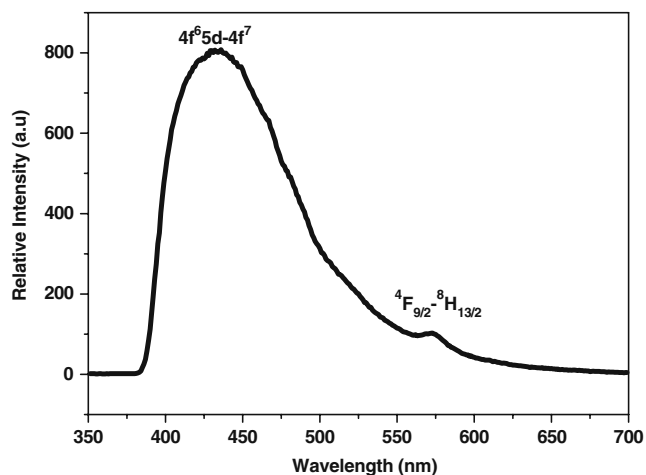


Fig. 2 The emission spectrum of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_{0.03}^{2+}, \text{Dy}_{0.01}^{3+}$ annealed at 1100°C for 4 h

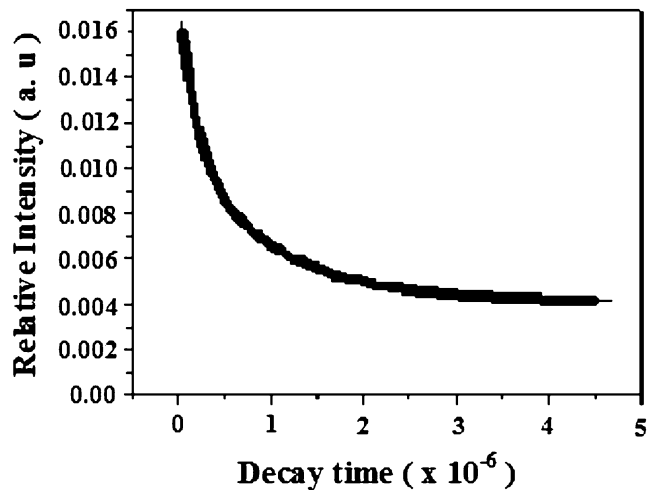


Fig. 4 The decay curve for the emission band of Eu^{2+} at 420 nm in the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_{0.03}^{2+}, \text{Dy}_{0.01}^{3+}$ sample

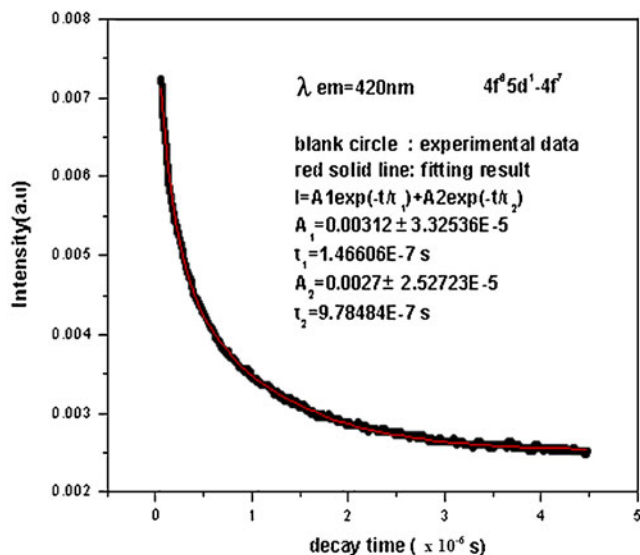


Fig. 5 The decay curve for the emission band of Eu^{2+} at 420 nm in the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_{0.03}^{2+}$

$\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}$ sample in Fig. 3. When the doping concentration of Dy^{3+} increased from 0 to 1 mol%, the luminescence intensity turned twice as strong as in the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}$ sample. When the Dy^{3+} concentration was further increased from 1 mol% to 1.25 mol% and 2 mol%, the emission intensity decreased greatly most probably due to concentration quenching. Thus, the best incorporation concentration of Dy^{3+} is 1 mol%. If the excitation energy is not transferred from Dy to Eu, the improvement of the phosphorescence intensity maybe due to the following reason: As the ions radius of Dy^{3+} (90.8 pm) is bigger than that of Y (89.3 pm) [15], the crystal parameters of the host will be deformed, and the surrounding ions of Eu^{2+} will also be changed when Dy is doped into $\text{YAl}_3(\text{BO}_3)_4$ crystal lattice. Many Eu^{2+} would be replaced by Dy^{3+} . These phenomena may decrease the non-radiative transition process and increase the phosphorescence intensity. As the phonon frequencies of the surroundings were also changed, a decrease of non-radiative efficiency occurs when the phonon frequencies decrease, and vice versa.

Table 1 Effect of the content of Eu^{2+} and Dy^{3+} ions on the decay times of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor.

$\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_x^{2+}\text{Dy}_y^{3+}$		τ_1	τ_2
x	y		
0.03	0	0.168 μs	0.946 μs
0.03	0.005	0.165 μs	0.961 μs
0.03	0.0075	0.185 μs	0.098 μs
0.03	0.01	0.147 μs	0.978 μs
0.03	0.0125	0.154 μs	0.942 μs

Table 2 The decay time of $\text{MAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$ and $(\text{Sr}, \text{M})\text{Al}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$ (M=Ca, Ba) samples.

Host	Decay time (μs)
$\text{BaAl}_2\text{B}_2\text{O}_7$	2.16
$(\text{Ba}_{0.6}\text{Sr}_{0.4})\text{Al}_2\text{B}_2\text{O}_7$	1.81
$\text{SrAl}_2\text{B}_2\text{O}_7$	2.20
$(\text{Sr}_{0.6}\text{Ca}_{0.4})\text{Al}_2\text{B}_2\text{O}_7$	0.613
$\text{CaAl}_2\text{B}_2\text{O}_7$	0.586

3.2 Luminescence decay characteristics

The phosphorescence characteristics of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ are evaluated based on the decay times that have been calculated using a curve fitting technique. The decay curves of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ are fitted by the sum of two exponential components $I=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$, where

I is the phosphorescence intensity at anytime after switching-off illumination, A_1 and A_2 are constants, τ_1 and τ_2 are decay times for the exponential components, respectively.

Figures 4 and 5 show decay curves of $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}$, respectively. Both are well fitted with the two exponential sum functions, and exhibit two lifetimes: a fast one and a slow one. The decay times of the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}_{0.03}^{2+}, \text{Dy}_x^{3+}$ samples are listed in Table 1, the concentration of Dy^{3+} change from 0.01 mol % to 1.25 mol%. All are around 0.1 μs , which is much shorter than for most of Eu^{2+} doped materials. The decay times of Dy^{3+} in other host materials are listed in Table 2. [16].

As we mentioned above, most of the $\text{Eu}^{2+}, \text{Dy}^{3+}$ co-doped materials are long-persistence phosphors, the luminescence mechanism is interpreted as follows (Fig. 6): Dy^{3+} ions act as hole traps. The trap levels are situated between

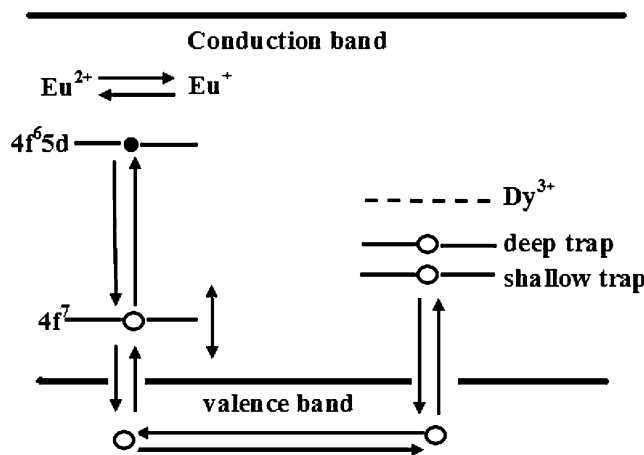


Fig. 6 Energy level diagram of the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor

the excited and ground states of Eu^{2+} . This is because the tetravalent state of Dy is stable. Moreover, Dy^{3+} possesses relatively higher transfer energies than any other trivalent rare earth ions. After excitation in the ultraviolet, electrons of Eu^{2+} in the 4f level transfer to a 5d level, and holes are produced in the 4f level; simultaneously at the same time, Eu^{2+} changes to Eu^+ . Some free holes created in the valence band of the host diffused to reach a certain distance. When the excitation source is turned off, holes captured by the Dy^{3+} hole traps are slowly thermally released, and return to the process described above [17–20]. Thus, along phosphorescence occurs. If the holes in the trap levels are too deep to be released at room temperature, the holes captured by Dy^{3+} will be ineffective to participate in the long phosphorescence process. The long phosphorescence process of Eu^{2+} , Dy^{3+} co-doped $\text{YAl}_3(\text{BO}_3)_4$ system belongs to the latter. Holes captured by Dy^{3+} are too deep to be released, so the materials display rapid decay characteristics. Moreover, when Dy^{3+} is doped into the $\text{YAl}_3(\text{BO}_3)_4$ crystal lattice, it induces some distortion, their fluorescence decay time to be much shorter causing compared to other Eu^{2+} doped $\text{YAl}_3(\text{BO}_3)_4$ materials.

4 Conclusions

$\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}$, Dy^{3+} samples are prepared by the sol-gel method. The samples are rapid decay phosphors. This feature is different than other Eu^{2+} , Dy^{3+} codoped materials as they are long-persistent phosphors. The experimental results show that the luminescence types of the samples are not only determined by activators, but also closely related to the hosts. The change of hosts or crystal parameters could influence the decay time of the samples. This conclusion makes transformation between the long-persistent phosphor and the rapid decay phosphor to be possible.

The incorporation of Dy^{3+} increases the $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}$ fluorescence intensity while simultaneously making the decay time of the samples much shorter than other blue fluorescence materials which accept Eu^{2+} as an activator. $\text{YAl}_3(\text{BO}_3)_4:\text{Eu}^{2+}$, Dy^{3+} sample with these characteristics is applied to plasma displays and especially to the display of

fast moving image, because if the decay time is not short enough the image will be dragged. We will synthesize the sample of $\text{BaMgAl}_{14}\text{O}_{23}:\text{Eu}^{2+}$, Dy^{3+} to further improve the properties of this commercially used material.

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