

Luminescence and energy transfer of white emitting phosphor $\text{YAl}_3(\text{BO}_3)_4:\text{Ce}^{3+}, \text{Dy}^{3+}$

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A white emitting phosphor of $\text{YAl}_3(\text{BO}_3)_4:\text{Ce}^{3+}, \text{Dy}^{3+}$ is synthesized by a solid state reaction, and its luminescent properties are investigated. Its phase formation is carried out with X-ray powder diffraction analysis, and there is no crystalline phase other than $\text{YAl}_3(\text{BO}_3)_4$. $\text{YAl}_3(\text{BO}_3)_4:\text{Ce}^{3+}$ can produce 422 nm blue emission under 367 nm excitation. The emission spectrum of $\text{YAl}_3(\text{BO}_3)_4:\text{Dy}^{3+}$ shows several emission peaks under 350 nm excitation, and the peaks locate at 485 nm, 575 nm and 668 nm, respectively. Emission intensities of Ce^{3+} and Dy^{3+} in $\text{YAl}_3(\text{BO}_3)_4$ are influenced by their concentrations, and the concentration quenching effect is observed. Energy transfer from Ce^{3+} to Dy^{3+} in $\text{YAl}_3(\text{BO}_3)_4$ is validated and proved to be a resonant type via a quadrupole-quadrupole interaction, and the emission color can be tuned from blue to white by tuning the ratio of $\text{Ce}^{3+}/\text{Dy}^{3+}$. Moreover, the critical distance (R_c) of Ce^{3+} to Dy^{3+} in $\text{YAl}_3(\text{BO}_3)_4$ is calculated to be 1.904 nm.

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White light-emitting diodes (white LEDs) have been considered to be important solid-state light sources. However, the white LEDs based on blue LED chip and $\text{YAG}:\text{Ce}^{3+}$ phosphor have high correlated color temperature ($CCT \approx 7\ 750$ K) and poor color rendering index ($CRI \approx 70-80$), because they are lack of red component. To avoid these disadvantages, the single-phase white emitting phosphors with high efficiency and long duration are investigated. Generally, trivalent dysprosium ion (Dy^{3+}) doped phosphors can create blue peak (${}^4\text{F}_{9/2}-{}^6\text{H}_{15/2}$) and yellow peak (${}^4\text{F}_{9/2}-{}^6\text{H}_{13/2}$), and the yellow emission can be tuned by chemical environment surrounding Dy^{3+} due to $\Delta J=2$ (${}^4\text{F}_{9/2}-{}^6\text{H}_{13/2}$), while the blue emission has invariable characteristics^[1]. Therefore, the Dy^{3+} doped phosphors can emit blue, yellow and white light by tuning the ratio of two dominant emission bands arising from ${}^4\text{F}_{9/2}-{}^6\text{H}_{15/2}$ (blue) and ${}^4\text{F}_{9/2}-{}^6\text{H}_{13/2}$ (yellow) transitions of Dy^{3+} ^[2]. Actually, the emission intensities of Dy^{3+} doped phosphors can be enhanced by energy transfer from donor (sensitizer, such as Ce^{3+}) to acceptor (activator) Dy^{3+} . Moreover, the emission color of Dy^{3+} doped phosphors can also be tuned by appropriately adjusting relative proportion of $\text{Ce}^{3+}/\text{Dy}^{3+}$ ^[3]. Generally, phosphors consist of activator and host. In order to obtain efficient

emission, the choice of host is another key factor, and the host must have excellent physical and chemical stability^[4]. As an important family of luminescent materials, borate compounds have attracted more and more attention^[5,6] because of simple synthesization condition, excellent thermal stability and strong absorption in the ultraviolet (UV) region. Li et al^[7] reported luminescence and thermal stability of $\text{Ba}_2\text{B}_2\text{O}_5:\text{Ce}^{3+}$. Yu et al^[8] achieved blue emitting phosphor $\text{Sr}_3(\text{BO}_3)_3\text{Cl}:\text{Ce}^{3+}$. Zhang et al^[9] synthesized blue emitting phosphor $\text{NaCaBO}_3:\text{Ce}^{3+}$ with high efficiency for UV LED. Dai et al^[10] investigated luminescence and energy transfer of $\text{Ce}^{3+}-\text{Tb}^{3+}$ in $\text{YAl}_3(\text{BO}_3)_4$. In this paper, we prepare a white emitting phosphor $\text{YAl}_3(\text{BO}_3)_4:\text{Ce}^{3+}, \text{Dy}^{3+}$, and explore its luminescence and energy transfer of $\text{Ce}^{3+}-\text{Dy}^{3+}$. The results may be helpful for UV based white LEDs.

The samples were synthesized by a high temperature solid-state reaction technique. According to the molecular formula of $\text{YAl}_3(\text{BO}_3)_4:x\text{Ce}^{3+}, y\text{Dy}^{3+}$, the raw materials of Y_2O_3 , Al_2O_3 , H_3BO_3 , CeO_2 and Dy_2O_3 , which are of analytical grade, were stoichiometrically weighed and thoroughly mixed in an agate mortar. The mixed powders were calcined in corundum crucibles at 1 300 °C for 4 h

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in air. Finally, the samples were cooled down to room temperature and ground thoroughly again into powders. Moreover, all the samples were sieved under the same condition to ensure the similar particle size distribution.

The phase formation was determined by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu K α 1 radiation ($\lambda=0.154\ 06\ \text{nm}$), and a scan rate of $0.02^\circ/\text{s}$ is applied to record patterns in the 2θ range from 10° to 80° . The spectral characteristics were detected by a fluorescence spectrophotometer (Hitachi F-4600), and the exciting source was a 450 W Xe lamp. Commission International de l'Eclairage (CIE) chromaticity coordinates of samples were measured by a PMS-80 spectra analysis system. All measurements were carried out at room temperature.

The XRD patterns of $\text{YAl}_3(\text{BO}_3)_4:x\text{Ce}^{3+}$, $y\text{Dy}^{3+}$ are measured as shown in Fig.1. It is obvious that the diffraction peaks of all the samples can be exactly assigned to pure phase of $\text{YAl}_3(\text{BO}_3)_4$ according to JCPDS No.15-0117. The uniform diffraction pattern means that the phase formation of $\text{YAl}_3(\text{BO}_3)_4$ is not influenced by a little amounts of Ce^{3+} , Dy^{3+} , or $\text{Ce}^{3+}/\text{Dy}^{3+}$. Fig.1 shows the XRD patterns of 0.03Ce^{3+} , 0.03Dy^{3+} and $0.03\text{Ce}^{3+}/0.03\text{Dy}^{3+}$ doped $\text{YAl}_3(\text{BO}_3)_4$, and the similar diffraction patterns are observed for each sample. $\text{YAl}_3(\text{BO}_3)_4$ has a hexagon crystal structure with a space group of $R\text{-}32$ (155), and the lattice parameters are $a=b=0.929\ 3\ \text{nm}$ and $c=0.724\ 5\ \text{nm}$.

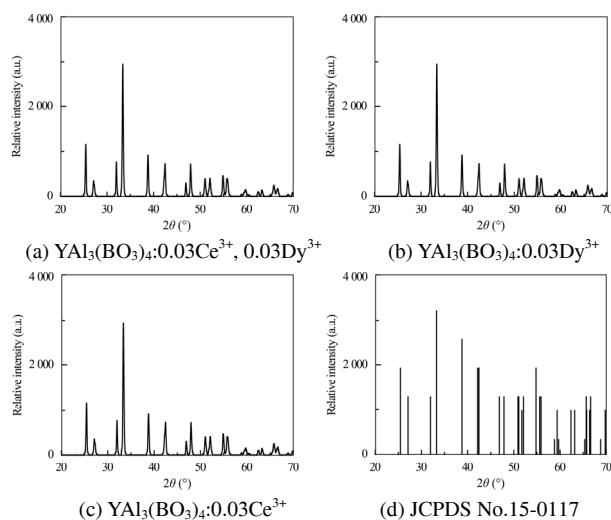


Fig.1 XRD patterns of $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Ce}^{3+}$, $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Dy}^{3+}$, $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Ce}^{3+}$, 0.03Dy^{3+} and $\text{YAl}_3(\text{BO}_3)_4$ (standard JCPDS No.15-0117)

Fig.2(a) depicts the excitation and emission spectra of $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Ce}^{3+}$. The excitation spectrum shows a broad excitation band, and the excitation peak locates at 367 nm, which corresponds to the transition from the Ce^{3+} 4f ground state ($^2\text{F}_{5/2}$) to the various 5d crystal-field component^[7,8]. Under 367 nm excitation, the emission spectra of $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Ce}^{3+}$ show two emission bands at 396 nm ($25\ 252\ \text{cm}^{-1}$) and 422 nm ($23\ 697\ \text{cm}^{-1}$),

and the energy difference between them is about $1\ 555\ \text{cm}^{-1}$. It is well known that Ce^{3+} emission should be composed of double bands in view of its ground state splitting, and the energy difference of splitting between $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ of Ce^{3+} is about $2\ 000\ \text{cm}^{-1}$ ^[7,8]. There is a small difference compared with the theoretical value of $2\ 000\ \text{cm}^{-1}$ for the $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ states, so one type of Ce^{3+} luminescence center exists in $\text{YAl}_3(\text{BO}_3)_4$.

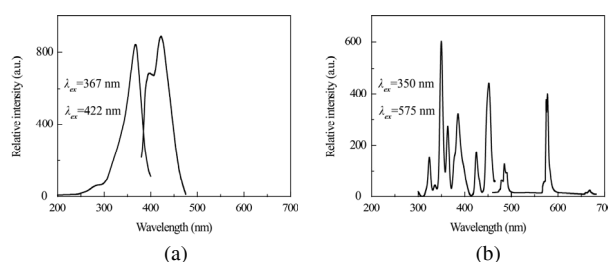


Fig.2 Emission and excitation spectra of (a) $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Ce}^{3+}$ and (b) $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Dy}^{3+}$

Fig.2(b) presents the emission and excitation spectra of $\text{YAl}_3(\text{BO}_3)_4:0.03\text{Dy}^{3+}$. Under 350 nm UV excitation, $\text{YAl}_3(\text{BO}_3)_4:\text{Dy}^{3+}$ shows several emission peaks, and the peaks locate at 485 nm, 575 nm and 668 nm, which are assigned to $^4\text{F}_{9/2}\rightarrow^6\text{H}_{15/2}$, $^4\text{F}_{9/2}\rightarrow^6\text{H}_{13/2}$ and $^4\text{F}_{9/2}\rightarrow^6\text{H}_{11/2}$ transitions of Dy^{3+} , respectively, and some emission bands show a splitting pattern, such as $^4\text{F}_{9/2}\rightarrow^6\text{H}_{15/2}$ transition of Dy^{3+} (479 nm and 485 nm)^[1,2]. For the emission bands, the yellow emission transition of $^4\text{F}_{9/2}\rightarrow^6\text{H}_{13/2}$ is dominant among the others, and $\text{YAl}_3(\text{BO}_3)_4:\text{Dy}^{3+}$ can create yellow emission under UV excitation. For the 575 nm emission, the excitation spectrum shows a series of narrow bands^[1,2] which belong to the intrinsic f-f transition of Dy^{3+} from the ground state $^6\text{H}_{15/2}$ to the excited states of $^6\text{P}_{7/2}$, $^6\text{P}_{5/2}$, $^4\text{I}_{13/2}$, $^4\text{G}_{11/2}$, $^4\text{I}_{15/2}$ and $^4\text{F}_{9/2}$, respectively. The obvious excitation peaks locate at 350 and 452 nm, so $\text{YAl}_3(\text{BO}_3)_4:\text{Dy}^{3+}$ can produce an obvious yellow emission under UV or blue radiation excitation.

In order to achieve the optimal concentration of Ce^{3+} or Dy^{3+} , a series of $\text{YAl}_3(\text{BO}_3)_4:x\text{Ce}^{3+}$ and $\text{YAl}_3(\text{BO}_3)_4:y\text{Dy}^{3+}$ ($x, y=0.005\text{--}0.07$) are synthesized, and the relative emission intensities are shown in Fig.3, respectively. The relative emission intensities have the similar trend with increasing Ce^{3+} or Dy^{3+} concentration. For example, the emission intensity of $\text{YAl}_3(\text{BO}_3)_4:x\text{Ce}^{3+}$ ($\lambda_{\text{ex}}=367\ \text{nm}$) firstly enhances with increasing Ce^{3+} concentration (x), and achieves a maximum at $x=0.03$, then decreases with further increasing its concentration because of the concentration quenching effect, in other words, the optimal concentration of Ce^{3+} is 0.03. For $\text{YAl}_3(\text{BO}_3)_4:y\text{Dy}^{3+}$ ($\lambda_{\text{ex}}=350\ \text{nm}$), the optimal concentration of Dy^{3+} is also 0.03.

Fig.2 presents that there is a significant spectral overlap between the emission band of $\text{YAl}_3(\text{BO}_3)_4:\text{Ce}^{3+}$ and the excitation band of $\text{YAl}_3(\text{BO}_3)_4:\text{Dy}^{3+}$, therefore, an effective resonant energy transfer is expected to occur from Ce^{3+} to Dy^{3+} . Under Ce^{3+} 367 nm excitation, the

emission spectra of $YAl_3(BO_3)_4:0.03Ce^{3+}, yDy^{3+}$ ($y=0-0.05$) are measured. As a representative, the inset of Fig.4 shows the emission spectrum of $YAl_3(BO_3)_4:0.03Ce^{3+}, 0.02Dy^{3+}$, and there are both Ce^{3+} and Dy^{3+} emission bands. In order to investigate the energy transfer from Ce^{3+} to Dy^{3+} , the normalized intensities of $YAl_3(BO_3)_4:0.03Ce^{3+}$ are recorded with increasing Dy^{3+} concentration, and Fig.4 shows that the emission intensities of Ce^{3+} obviously decrease with increasing Dy^{3+} concentration. Moreover, Fig.5 presents the emission spectra of $YAl_3(BO_3)_4:xCe^{3+}, 0.03Dy^{3+}$ ($x=0, 0.01, 0.03$). It can be seen from Fig.5 that although the Dy^{3+} concentration is fixed, the emission intensities of Dy^{3+} dramatically enhance with increasing Ce^{3+} concentration, which further supports the energy transfer from Ce^{3+} to Dy^{3+} .

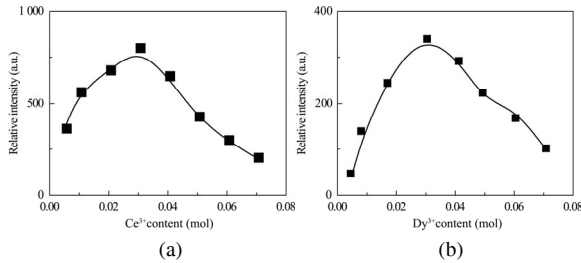


Fig.3 Emission intensities as a function of impurity (a) Ce^{3+} and (b) Dy^{3+} concentrations

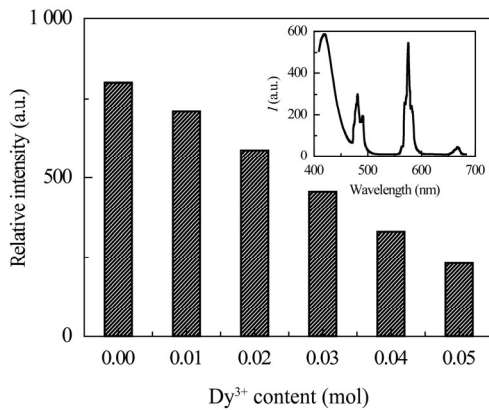


Fig.4 Emission intensities of Ce^{3+} as a function of Dy^{3+} concentration (The inset is the emission spectrum of $YAl_3(BO_3)_4:0.03Ce^{3+}, 0.02Dy^{3+}$ with $\lambda_{ex}=367$ nm.)

For $YAl_3(BO_3)_4:0.03Ce^{3+}, yDy^{3+}$ ($y=0-0.05$), the energy transfer efficiency (η_T) can be achieved by^[11]

$$\eta_T = 1 - (I_S / I_{S0}), \quad (1)$$

where I_{S0} and I_S are luminescent intensities of sensitizer Ce^{3+} in the absence and presence of activator Dy^{3+} , respectively. Consequently, the variation of η_T for $YAl_3(BO_3)_4:0.03Ce^{3+}, yDy^{3+}$ ($y=0-0.05$) with Dy^{3+} content is shown in Fig.6. It can be seen that the energy transfer efficiency continuously enhances with increasing Dy^{3+} concentration, and the energy transfer efficiency is observed as 71.13%.

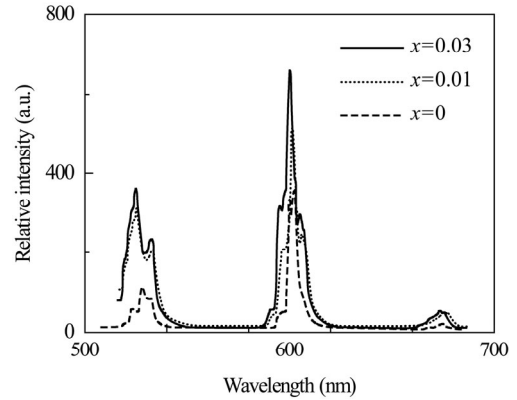


Fig.5 Emission spectra of $YAl_3(BO_3)_4:xCe^{3+}, 0.03Dy^{3+}$ ($\lambda_{ex}=367$ nm)

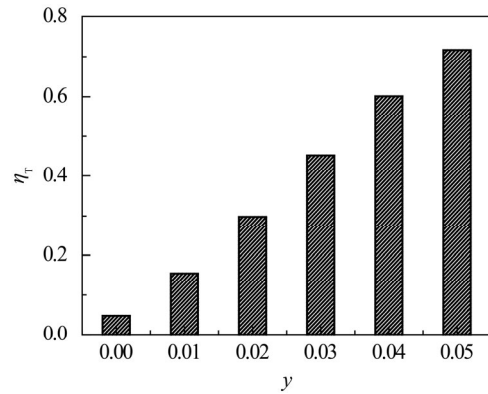


Fig.6 Dependence of energy transfer efficiency η_T on Dy^{3+} content y

It has been well known that the non-radiative energy transfer in oxalic phosphors is based on the resonance transfer by electric multipole-multipole interaction or exchange interaction. If the distance between activators is larger than 0.5 nm, the exchange interaction becomes ineffective, and only the electric multipole-multipole interaction is important^[12]. Thus, it is necessary to obtain the critical distance (R_c) which is the critical separation between the activator and the quenching site. According to Ref.[12], R_c can be calculated by the critical concentration of activator ion as

$$R_{Ce-Dy} = [3V / (4\pi x_c N)]^{1/3}, \quad (2)$$

where x_c is the sum concentration of Ce^{3+} and Dy^{3+} , N is the number of Z ions in the unit cell (for $YAl_3(BO_3)_4$, $N=3$), and V is the volume of unit cell (for $YAl_3(BO_3)_4$, $V=0.54185$ nm³).

The estimated distances of R_{Ce-Dy} for $YAl_3(BO_3)_4:0.03Ce^{3+}, yDy^{3+}$ with $x_c=0.03, 0.04, 0.05, 0.06, 0.07$ and 0.08 are 2.257 nm, 2.051 nm, 1.904 nm, 1.791 nm, 1.702 nm and 1.628 nm, respectively. The distance between Ce^{3+} and Dy^{3+} becomes shorter with increasing Dy^{3+} concentration. x is the critical concentration at which emission intensity of donor (Ce^{3+}) in the presence of acceptor (Dy^{3+}) is half of that in the absence of acceptor (Dy^{3+}). Therefore, R_c of energy transfer is calculated to

be about 1.904 nm for $YAl_3(BO_3)_4:0.03Ce^{3+}, yDy^{3+}$. R_{Ce-Dy} for various Ce^{3+} content levels is much larger than the typical critical distance for exchange interaction (0.5 nm)^[12]. This means that exchange interaction plays no role in energy transfer process for $YAl_3(BO_3)_4:Ce^{3+}, Dy^{3+}$. Therefore, the energy transfer between Ce^{3+} and Dy^{3+} exists in $YAl_3(BO_3)_4$, and the emission intensity of Dy^{3+} is enhanced by efficient energy transfer from Ce^{3+} to Dy^{3+} , which belongs to the multipolar interaction. On the basis of Dexter's energy transfer formula for multipolar interactions, the following relation can be obtained^[13]

$$(\eta_0 / \eta) \propto C^{\alpha/3}, \quad (3)$$

where η_0 and η are luminescence quantum efficiencies of Ce^{3+} in the absence and presence of Dy^{3+} , respectively, and C is the total concentration of Ce^{3+} and Dy^{3+} . Eq.(3) with $\alpha=6, 8$ and 10 belongs to dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively. The relationship of $(I_{S0}/I_S) \propto C^{\alpha/3}$ is illustrated in Fig.7. The linear relationship reaches the optimal one for $(I_{S0}/I_S) \propto C^{\alpha/3}$ by comparing the fitting factor of R value. It can be seen from Fig.7(c) that the energy transfer from Ce^{3+} to Dy^{3+} occurs via the quadrupole-quadrupole interaction.

Color coordinate is one of the important factors for evaluating the performance of phosphors^[14,15]. The color coordinates of $YAl_3(BO_3)_4:xCe^{3+}, yDy^{3+}$ are measured and shown in Tab.1. And the chromatic standard is issued by the CIE in 1931 (CIE 1931). It can be seen that the

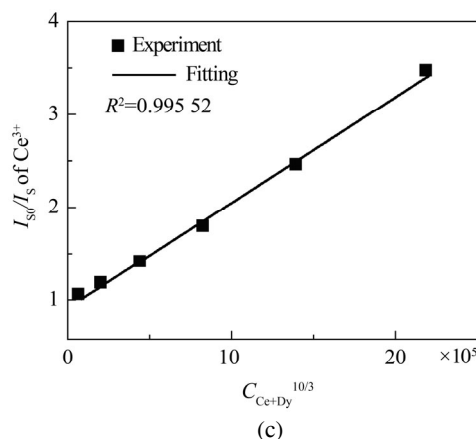


Fig.7 Dependence of I_{S0}/I_S on $C^{\alpha/3}$ with (a) $\alpha=6$ for dipole-dipole interaction, (b) $\alpha=8$ for dipole-quadrupole interaction and (c) $\alpha=10$ for quadrupole-quadrupole interaction

color coordinates of $YAl_3(BO_3)_4:xCe^{3+}, yDy^{3+}$ are approximately in the white region. For example, the CIE color coordinates of $YAl_3(BO_3)_4:0.03Ce^{3+}, 0.03Dy^{3+}$ are (0.293 9, 0.283 6). It means that $YAl_3(BO_3)_4:Ce^{3+}, Dy^{3+}$ may have potential application as white emitting phosphor for white LEDs.

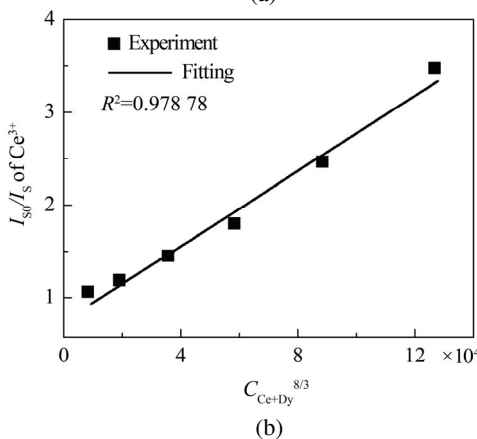
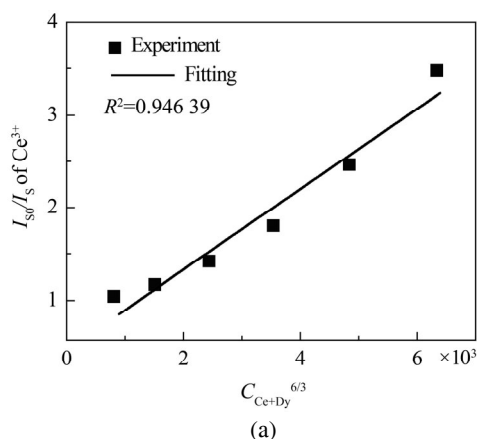
Tab.1 CIE coordinates of $YAl_3(BO_3)_4:xCe^{3+}, yDy^{3+}$ ($\lambda_{ex}=365$ nm)

Sample	CIE (X, Y)
$YAl_3(BO_3)_4:0.03Ce^{3+}$	(0.162 1, 0.017 9)
$YAl_3(BO_3)_4:0.03Ce^{3+}, 0.02Dy^{3+}$	(0.291 6, 0.279 8)
$YAl_3(BO_3)_4:0.03Ce^{3+}, 0.05Dy^{3+}$	(0.299 5, 0.287 9)
$YAl_3(BO_3)_4:0.03Dy^{3+}$	(0.383 6, 0.401 2)
$YAl_3(BO_3)_4:0.01Ce^{3+}, 0.03Dy^{3+}$	(0.276 2, 0.273 9)

A white emitting phosphor of $YAl_3(BO_3)_4:Ce^{3+}, Dy^{3+}$ is synthesized by a solid state reaction. The energy transfer from Ce^{3+} to Dy^{3+} in $YAl_3(BO_3)_4$ is validated and proved to be a resonant type via a quadrupole-quadrupole interaction, and the critical distance R_c of Ce^{3+} to Dy^{3+} in $YAl_3(BO_3)_4$ is calculated to be 1.904 nm. Moreover, the emission intensities of $YAl_3(BO_3)_4:Dy^{3+}$ can be obviously enhanced by using co-doped Ce^{3+} as sensitizer, and the emission color of $YAl_3(BO_3)_4:Ce^{3+}, Dy^{3+}$ can be tuned from blue to white by tuning the ratio of Ce^{3+}/Dy^{3+} . The results indicate that $YAl_3(BO_3)_4:Ce^{3+}, Dy^{3+}$ may serve as potential white emitting material for white LEDs.

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