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Influence of energy transfer from Ce^{3+} to Eu^{2+} on luminescence properties of $Ba_3Si_6O_9N_4$:Ce^{3+}, Eu^{2+} phosphors

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Abstract

$Ba_3Si_6O_9N_4$ phosphors co-doped with Ce^{3+} and Eu^{2+} were synthesized via the solid-state reaction method. The samples could display varied color emission from blue and ultimately to green under the excitation of ultraviolet (UV) light or blue light with the appropriate adjustment of the relative proportion of Ce^{3+}/Eu^{2+}. The luminescence intensity of $Ba_3Si_6O_9N_4$:Eu^{2+} can be efficiently enhanced by codoping with Ce^{3+}. The energy transfer mechanism from Ce^{3+} to Eu^{2+} in $Ba_3Si_6O_9N_4$:Ce^{3+}, Eu^{2+} is electric dipole–dipole interaction, and the critical distance is calculated to be about 24.86 Å by the spectra overlap method.

Keywords: $Ba_3Si_6O_9N_4$:Ce^{3+}, Eu^{2+}; Phosphors; Luminescence; Energy transfer

1. Introduction

The invention of phosphor converted white light emitting diodes (LEDs) has completely changed our life. It has brought a great revolution to the illumination. Compared with the conventional fluorescent, phosphors have excellent properties such as low power consumption, high efficiency, long life and of no mercury toxic performance [1,2], which are considered as the next-generation light source. Phosphors play an important role in improving the luminescence efficiency, intensity and life time. Therefore, multiple phosphors and blue or ultraviolet(UV) chips consisting of white LEDs, such as RGB (red, green and blue phosphor)/UV chip or RG/blue chip, have attracted increasing attention due to their excellent color rendering index (CRI) and high color tolerance [3,4].

At present, available commercial white LEDs are fabricated by the combination of blue-emitting InGaN-based LED chip and yellow-emitting YAG:Ce^{3+} phosphors [5]. However, the YAG:Ce^{3+} based white LED has a poor color rendering index (CRI) due to the lack of red light contribution. Thus, it is a particularly essential work to enhance the red emission of the photoluminescence spectra of white LEDs. The most commonly used method is via the physical mixing phosphors, such as yellow/red phosphors, green/red phosphors, or green/yellow/red phosphors [6–8]. So, it is urgent to search for a novel green or red-emitting phosphor.

Recently, the structure of a novel $Ba_3Si_6O_9N_4$:Eu^{2+} phosphor materials has been studied [9]. Nevertheless, the luminescence properties of single Ce^{3+}-doped and Ce^{3+}/Eu^{2+}-codoped $Ba_3Si_6O_9N_4$ phosphors have not been reported. In our present work, we investigate its photoluminescence (PL) properties as well as Energy transfer (ET) phenomenon between the sensitizer and activator, aiming at exploring a novel and applicable phosphor for white LEDs. It was found that the luminescence intensity of the $Ba_3Si_6O_9N_4$:Eu^{2+} phosphors can be efficiently enhanced by codoping with Ce^{3+}.

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2. Experimental

Ce^{3+}/Eu^{2+} co-activated $Ba_3Si_6O_9N_4$ phosphor was synthesized by the conventional solid-state reaction method at 1350 °C for 6 h under flowing reduction atmosphere of 90% N_2/10% H_2, using fine powders of high purity (> 99.99%) of SiO_2, $BaCO_3$, K_2CO_3, Si_3N_4, Eu_2O_3, CeO_2 as raw materials. For the sample doping of Ce^{3+} lions, K^+ ions were also used for charge compensation. Finally, the samples were obtained by grinding fully in an agate mortar after cooling to room temperature naturally.

The phase composition and crystallinity of the synthesized compositions were investigated by powder X-ray diffraction (XRD) (Bruker Axs D2 PHASER diffractometer, Cu kα = 0.15406 nm). The excitation and emission spectra of the phosphors were measured at room temperature on a PL3-211-P spectrometer (HORIBA JOBIN YVON, America) and a 450 W xenon lamp was used as the excitation source.

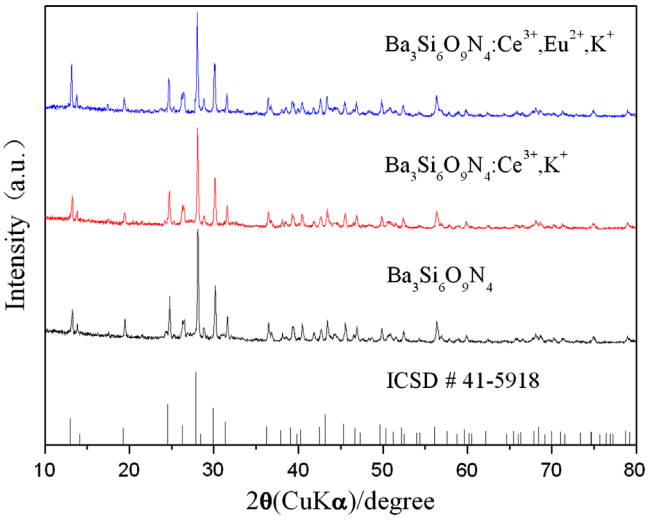

Fig. 1. XRD patterns of $Ba_3Si_6O_9N_4$, $Ba_3Si_6O_9N_4$:Ce^{3+}, K^+ and $Ba_3Si_6O_9N_4$:Ce^{3+}, Eu^{2+}, K^+ phosphors.

3. Results and discussion

The XRD patterns of $Ba_3Si_6O_9N_4$, $Ba_3Si_6O_9N_4$:Ce^{3+} K^+ and $Ba_3Si_6O_9N_4$:Ce^{3+} Eu^{2+} K^+ series' phosphors are presented in Fig. 1. All the diffraction peaks of the samples agree well with those of the standard patterns of $Ba_3Si_6O_9N_4$ (ICSD # 41-5918). The XRD results indicate that doping of Ce^{3+} and Eu^{2+} ions do not cause any significant change in the host structure, which clearly suggests that the activator and co-activator have been incorporated in the lattice.

$Ba_3Si_6O_9N_4$ crystallizes as a trigonal structure with lattice constants of $a = 7.2488$ Å, $c = 6.7836$ Å, and V (cell volume) = 308.69(9) Å^3. The crystal structure of $Ba_3Si_6O_9N_4$ is depicted in Fig. 2. In the structure of $Ba_3Si_6O_9N_4$, the Ba^{2+} ions have three different coordination environments: Ba(1), Ba (2) and Ba(3) [9]. Because of the similarities of their ionic radii, Eu^{2+} ion is expected to randomly occupy the Ba^{2+} ion sites in the $Ba_{3-x}Si_6O_9N_4$:xEu^{2+} crystal structure.

Fig. 3 shows the excitation and emission spectrums of the obtained $Ba_3Si_6O_9N_4$:$0.1Eu^{2+}$ phosphor. The excitation band of the $Ba_3Si_6O_{12}N_2$:$0.1Eu^{2+}$ phosphor ranged from 280–500 nm matches well with blue-emitting LEDs or near UV-emitting LEDs. The excitation band is attributed to the 4f–5d transition of the doped Eu^{2+} ions. The emission spectrum peaked at 520 nm with the full-width half-maximum (FWHM) of 78 nm is attributed to the $4f^65d^1$–$4f^7$ transition of the Eu^{2+} ion.

Fig. 4 shows the emission spectra of different concentration of Eu^{2+}/Ce^{3+} ions co-activated $Ba_3Si_6O_9N_4$ phosphors. However, for all the different concentration, the positions of peak in emission spectrums is nearly the same. One of the most important observations is the enhancement of the emission intensity with the increasing of co-activated concentration. The emission intensity of $Ba_{2.9-2y}Eu_{0.1}Ce_yK_ySi_6O_9N_4$ reaches to the maximum when the concentration of Eu^{2+} and Ce^{3+} are 0.1 and 0.01, respectively. It is obvious that emission intensity of the $Ba_3Si_6O_9N_4$:Eu^{2+} phosphors are enhanced about 198% by co-doped with Ce^{3+}, which can be attributed to the energy transfer from Ce^{3+} to Eu^{2+} in the host lattice of phosphor samples.

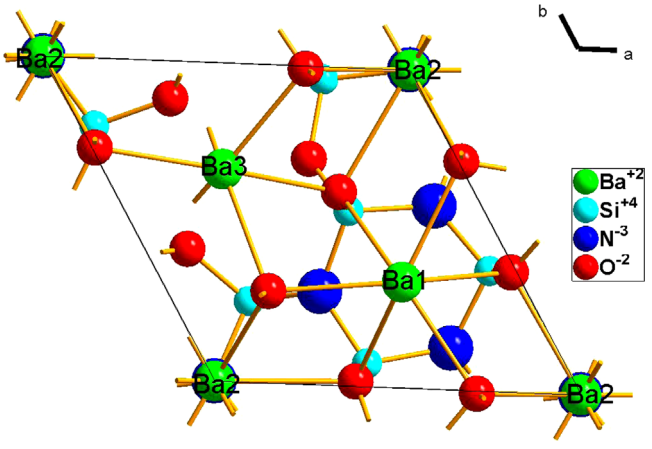

Fig. 2. Schematic views of the structure of $Ba_3Si_6O_9N_4$, solid line denotes the unit cell.

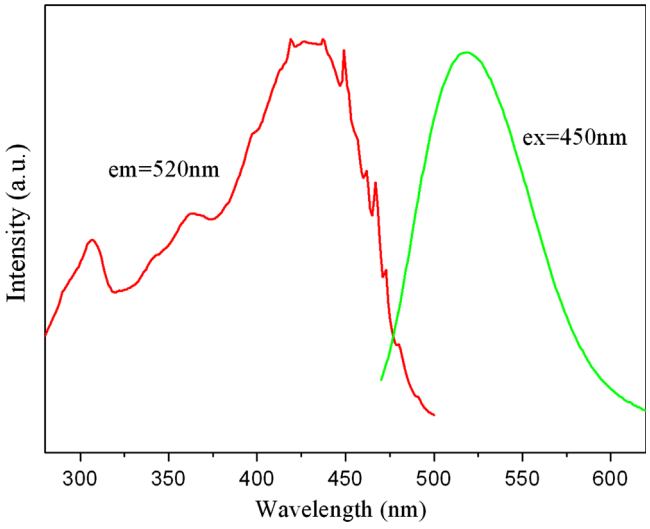

Fig. 3. Excitation and emission spectra of $Ba_3Si_6O_9N_4$:$0.1Eu^{2+}$ phosphor.

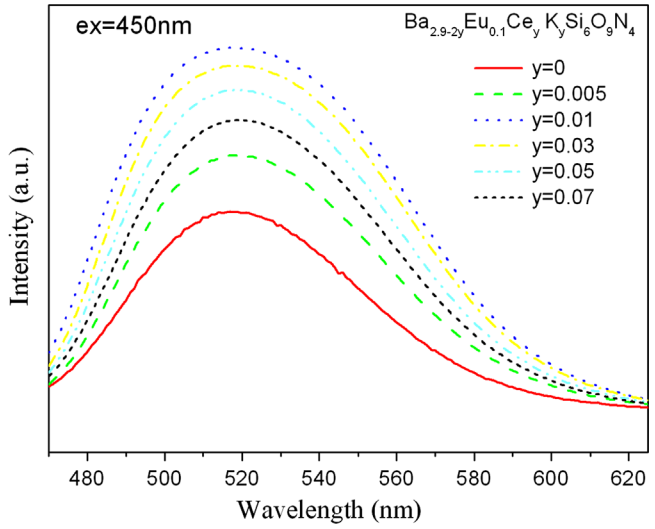

Fig. 4. Photoluminescence emission (PL) spectra of $Ba_{2.9-2y}Eu_{0.1}Ce_y K_ySi_6O_9N_4$ (from $y=0$ to $y=0.07$).

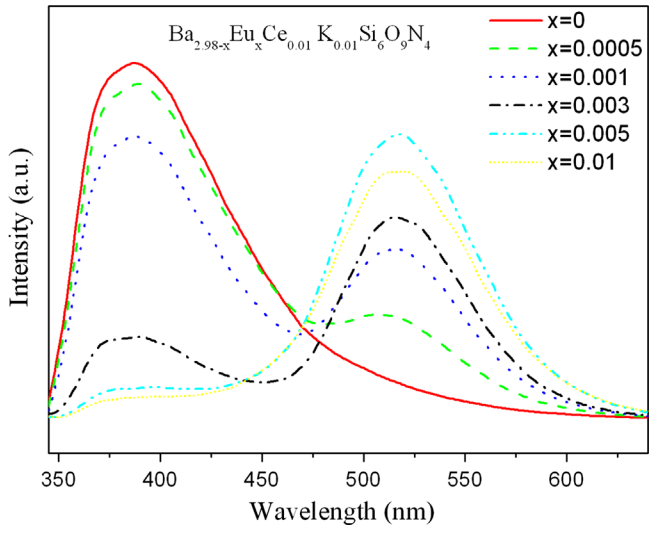

Fig. 5. Photoluminescence emission (PL) spectra of $Ba_{2.9-x}Eu_xCe_{0.01}K_{0.01}Si_6O_9N_4$ phosphors excited at 340 nm (from $x=0$ to $x=0.01$).

Fig. 5 shows the emission (PL) spectra of co-doped phosphors with formula of $Ba_{2.9-x}Eu_xCe_{0.01}K_{0.01}Si_6O_9N_4$ (from $x=0$ to $x=0.01$), upon 340 nm excitation. The intensity of the blue band, attributed to Ce^{3+} sensitizer, decayed over increasing Eu^{2+} content. The opposite occurred in the green band, which is attributed to the Eu^{2+} activator. Similar behavior has been reported for Ce^{3+} and Eu^{2+} co-doped silicates [10,11], borates [12,13], and sulfides [14], attributed to efficient energy transfer from Ce^{3+} to Eu^{2+}. The energy transfer efficiency (η_T) from Ce^{3+} to Eu^{2+} ions can be expressed by [15,16]:

$$\eta_T = 1 - \frac{I_S}{I_{S0}} \tag{1}$$

where I_{S0} and I_S are the luminescence intensities of sensitizer (Ce^{3+}) without and with activator (Eu^{2+}) present, respectively. Using the spectrums of Fig. 5, the values of η_T were calculated

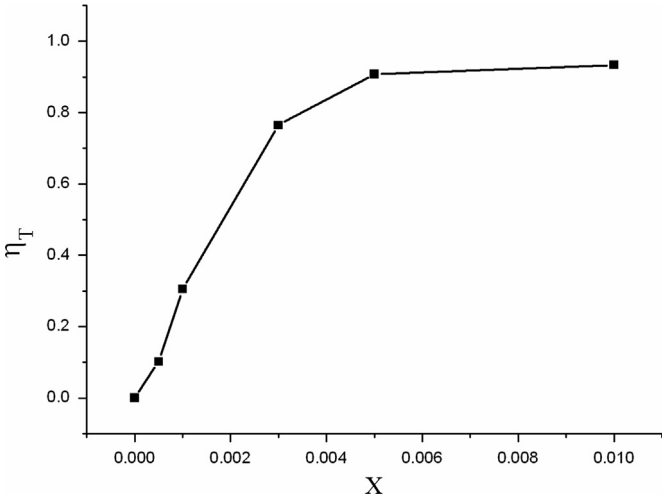

Fig. 6. Dependence of the energy transfer efficiency η_T in $Ba_{2.9-x}Eu_xCe_{0.01}K_{0.01}Si_6O_9N_4$ on x (from $x=0$ to $x=0.01$).

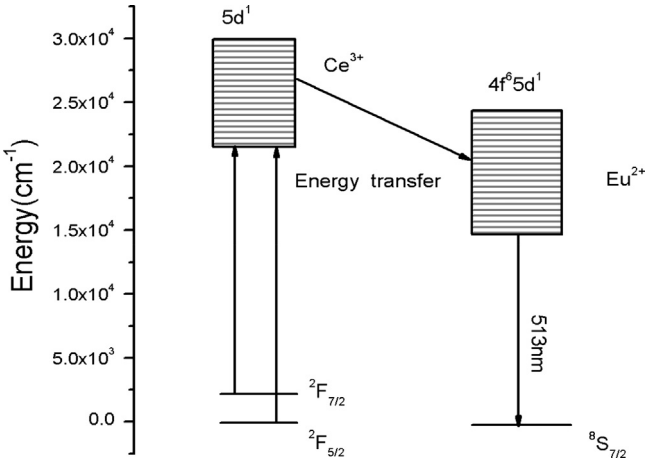

Fig. 7. Schematic of the energy level system describing energy transfer in the $Ba_3Si_6O_9N_4$:Ce^{3+}, Eu^{2+}, K^+ phosphor.

and the results are plotted in Fig. 6, in which η_T was found to increase with the increasing Eu^{2+} content (x). Meanwhile, the schematic diagrams for the energy levels of Ce^{3+} and Eu^{2+} and the energy transfer from Ce^{3+} to Eu^{2+} are both shown in Fig. 7.

According to the Dexter's energy transfer formula of multipolar interactions and Reisfeld's approximation, relationship (2) is valid [15–17,18]

$$\frac{N_0}{N} \propto C^{n/3} \tag{2}$$

where N_0 and N are the luminescence quantum efficiencies of Ce^{3+} in the absence and the presence of Eu^{2+}, respectively, and c is the Eu^{2+} content. The value of n depends on the type of interactions; specifically $n=6$ for dipole–dipole, $n=8$ for dipole–quadrupole, and $n=10$ for quadrupole–quadrupole interactions. The ratio N_0/N is approximately calculated by

$$\frac{I_{S0}}{I_S} \propto C^{n/3} \tag{3}$$

Using the data from Fig. 6, the three diagrams of Fig. 8 show the plots of relationship (3) for the three different values of n. The

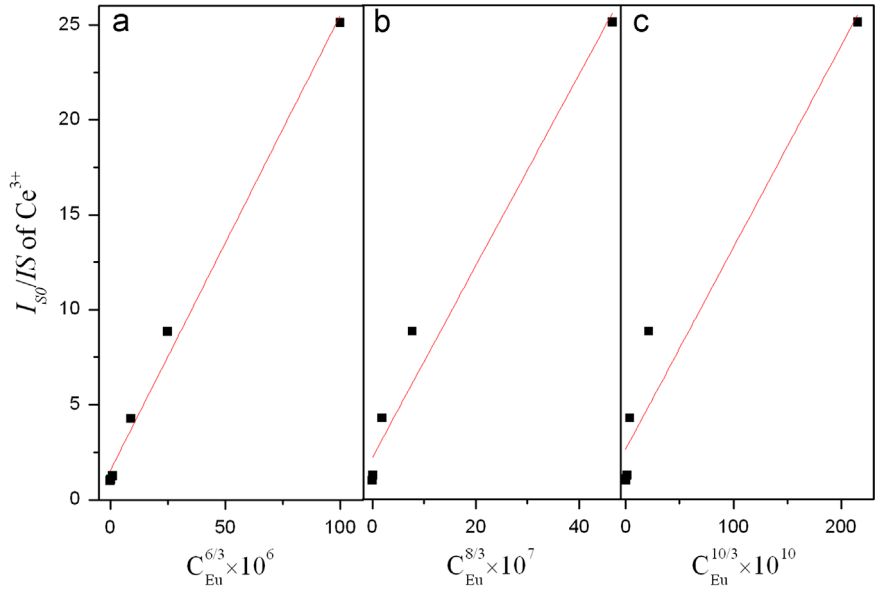

Fig. 8. Plots of I_{S0}/I_S vs. $C_{Eu}^{n/3}$ for (a) $n=6$, (b) $n=8$, and (c) $n=10$.

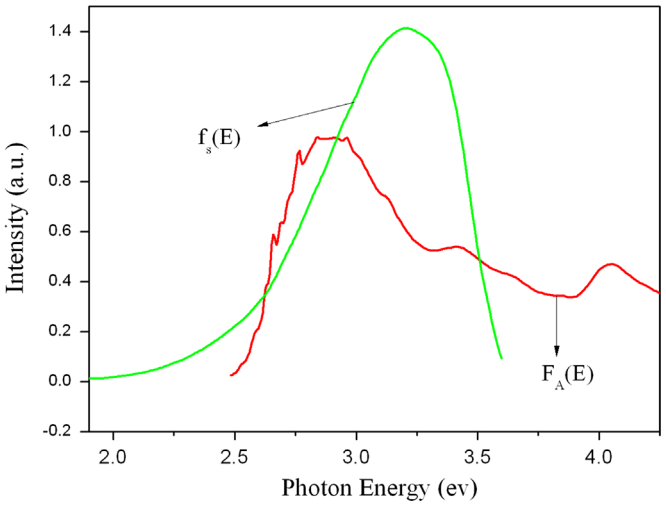

Fig. 9. Normalized line-shape functions for the Ce^{3+} emission [$f_s(E)$] and Eu^{2+} excitation [$F_A(E)$].

plots illustrated in Fig. 8(a) and (b) both exhibit linear relationships; moreover, electric dipole–dipole interaction usually accompanies electric dipole–quadrupole interaction because the Coulombic effect of the former is larger than that of the latter. Therefore, the electric dipole–dipole interaction predominates in the ET mechanism from Ce^{3+} to Eu^{2+} in $Ba_3Si_6O_9N_4$:Ce^{3+} Eu^{2+} K^+ which is similar to the result previously reported [19,20].

The $4f\rightarrow5d$ transition of Ce^{3+} and Eu^{2+} ions is an allowed one, hence, the energy transfer from Ce^{3+} to Eu^{2+} ions is predominantly attributed to the electric dipole–dipole interaction according to the theory of energy transfer of Dexter [21]. Therefore, the critical transfer distance (R_c) can be expressed as the following equation [22,23]:

$$R_c^6 = 3.0\times10^{12} f_d \int \frac{f_S(E)F_A(E)}{E^4}dE \quad (4)$$

where f_d=0.02 is the electric dipole oscillator strength for Eu^{2+}. The term $\int f_S(E)F_A(E)dE$ represents the spectral overlap between the normalized shapes of Ce^{3+} emission ($f_s(E)$) and Eu^{2+} excitation ($F_A(E)$) showed in Fig. 9, and it is calculated to be about 0.624 eV^{-1}. And E is the maximum energy of spectral overlap calculated (from Fig. 9) as 3.51 eV. Therefore, the R_c of ET $_{Ce\rightarrow Eu}$ was calculated to be about 24.86 Å.

4. Conclusions

The energy transfer between Eu^{2+} and Ce^{3+} in $Ba_3Si_6O_9N_4$ host has been discussed. The emission peak at 520 nm of $Ba_3Si_6O_9N_4$:Eu^{2+} is intensified by Ce^{3+} co-doping. When excited by ultraviolet of 340 nm, the $Ba_3Si_6O_9N_4$:Ce^{3+}, Eu^{2+}, K^+ phosphors have peak positions at 390 nm and 520 nm. The emission peak for the $4f^65d\rightarrow4f^7$ transition of Eu^{2+} is intensified by Ce^{3+} codoped, which confirms that an efficient energy transfer occurs from Ce^{3+} to Eu^{2+} in $Ba_3Si_6O_9N_4$, and the type is proved to be electric dipole–dipole interaction. Finally, it is obvious that emission intensity of the $Ba_3Si_6O_9N_4$:Eu^{2+} phosphors is enhanced about 198% by co-doping with Ce^{3+}. So $Ba_3Si_6O_9N_4$:Eu^{2+} co-doped with Ce^{3+} with considerable enhanced emission intensity can be useful for white LEDs.

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