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Single-phased emission-tunable $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} phosphors for white light-emitting diodes

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Abstract

A series of single-phased emission-tunable $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} phosphors has been prepared by the solid-state reaction method. The phosphors show two intense emission bands at about 450 nm and 610 nm, which are attributed to the 5d → 4f transitions of Ce^{3+} and Eu^{2+} ions, respectively. The emission colors of $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} phosphors vary from blue (0.148, 0.147) to white (0.309, 0.260), and eventually to orange (0.407, 0.319) by tuning the Eu^{2+}/Ce^{3+} ratio. Energy transfer from Ce^{3+} to Eu^{2+} is studied by luminescence spectra and energy transfer efficiency. The results show an electric quadrupole–quadrupole interaction plays an important role in the process of energy transfer. The phosphors with tunable emission are suitable for application in white light-emitting diodes.

Keywords: Phosphors; Luminescence; Energy transfer; Emission-tunable

1. Introduction

Light emitting diodes (LEDs) are considered as ideal candidates to replace conventional lighting sources due to their energy saving, high brightness, long lifetime and environmental friendly nature [1,2]. The commercial white LEDs consist of InGaN blue LED and Ce^{3+}-doped yttrium aluminum garnet yellow phosphors. Although preparation method of commercial white LEDs is inexpensive and efficient, the product has low color rendering index (CRI) due to the scarcity of the red emission, and poor color stability due to different degradation rates of chip and phosphor. To improve the color stability and obtain high CRI (> 85), white LEDs fabricated with near-ultraviolet (n-UV) LED chips and tricolor phosphors have received lots of attention in solid state lighting area due to tunable color temperature and high CRI [3].

Although white LEDs based on n-UV LED chips are expected to dominate the market in the near future, there are some drawbacks to be overcome. Commercial red phosphors suitable for n-UV LEDs are mainly focused on the nitride system which synthetic process is costly and intricate [4,5]. In addition, undesirable color aberration appears in the real application because of the difference in color degradations of different phosphors. One solution to these problems is to search for a single-host phosphor with blue, green and red emissions [6]. The single-host phosphor has usually sensitizers and activators, such as Ce^{3+}/Mn^{2+}, Ce^{3+}/Eu^{2+} and Eu^{2+}/Mn^{2+} [7–9]. The phosphor could exhibit varied hues by tuning the contents of sensitizers and activators due to the energy transfer from sensitizers to activators.

$Ca_3Si_2O_7$ phosphor is an important luminescent material, and has great potential application in LEDs because of its intense emission, environmental benignity, and excellent chemical and physical stabilities [10,11]. Although $Ca_3Si_2O_7$:Ce^{3+}, $Ca_3Si_2O_7$:Tb^{3+} and $Ca_3Si_2O_7$:Eu^{2+} have been prepared, and can emit intense visible light, the luminescence properties and energy transfer mechanism of Ce^{3+}, Eu^{2+} co-doped $Ca_3Si_2O_7$ phosphor is rarely reported [12]. In the present study, we report an emission-tunable phosphor, Ce^{3+}, Eu^{2+} co-doped $Ca_3Si_2O_7$, which shows intense absorption and emission. The energy

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transfer mechanism between Ce^{3+} and Eu^{2+} ions in the host lattice is investigated in detail.

2. Experimental

2.1. Sample preparation

The compound $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} was prepared by high temperature solid-state reaction in a horizontal tube furnace, in which $CaCO_3$ (AR), SiO_2 (AR), Eu_2O_3 (99.9%) and CeO_2 (99.9%) were used as starting materials. According to the given stoichiometric ratio, starting materials were mixed and ground in an agate mortar, as H_3BO_3 was added as a flux to improve phase purity and luminescent efficiency of the phosphors. After being filled into corundum crucibles, the mixture was preheated at 1000 °C for 5 h in an air atmosphere. After being reground, the samples were fired at 1200 °C for 12 h and at 1300 °C for 12 h in a reducing atmosphere of 5:95 (volume) H_2/N_2, then, cooled down to room temperature spontaneously. The sample was obtained as an orange powder.

2.2. Measurement and characterization

The phase purity was examined by powder X-ray diffraction (XRD) using a Bruker D2 powder diffractometer with Cu Kα radiation (30 kV × 10 mA). XRD data was collected in the 2θ range from 20° to 60° with 0.04°/step and a counting time of 30 s/step. The emission and excitation spectra were measured at room temperature using a Cary Eclipse fluorescence spectrophotometer with a Xe flash lamp as the excitation source. The Commission International de I'Eclairage (CIE) chromaticity coordinates were calculated by the spectra data. The surface morphologies were observed using a Phenom G2 pro high resolution desktop scanning electron microscope (SEM).

3. Results and discussion

3.1. XRD patterns

The powder XRD pattern of $Ca_3Si_2O_7$:$0.02Ce^{3+}$, $0.006Eu^{2+}$ sample is shown in Fig. 1, which indicates that the phosphor exists mostly as the typical $Ca_3Si_2O_7$ phase (JCPDS card no. 76-0623). However, a little impurity phase can be observed in the XRD pattern, which can be indexed as $CaSiO_3$. The spectrum indicates that Ce^{3+} and Eu^{2+} ions do not change $Ca_3Si_2O_7$ crystalline phase significantly, which should be ascribed to the successful introduction of lanthanide ions into host lattices according to ionic radii matching mechanism, because Ce^{3+} (1.01 Å), Eu^{2+} (1.17 Å) and Ca^{2+} (1.00 Å) ions have similar radii in the same host lattice [11]. The $Ca_3Si_2O_7$ compound was reported to be monoclinic with lattice constants $a=10.557$ Å, $b=8.885$ Å, $c=7.858$ Å, $\beta=119.586°$, $V=640.969$ Å^3, and $Z=4$ [13]. According to the given XRD data in Fig. 1, the lattice parameters of $Ca_3Si_2O_7$:$0.02Ce^{3+}$, $0.006\,Eu^{2+}$ were calculated by the JADE 5.0 software, and were $a=10.512$ Å, $b=8.903$ Å, $c=7.893$ Å, $\beta=118.670°$, and $V=648.127$ Å^3. The above results indicate that Ce^{3+} and Eu^{2+} ions are dissolved in the $Ca_3Si_2O_7$ host lattice, and lead to slight expansion of lattice volume due to large ionic radii of Ce^{3+} and Eu^{2+}.

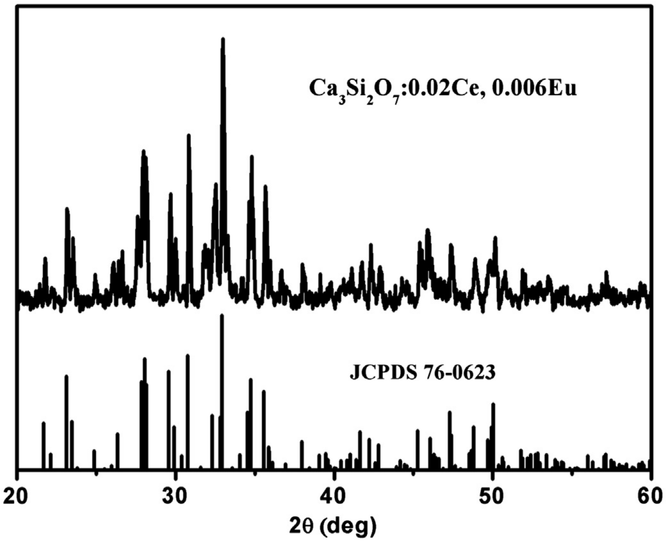

Fig. 1. XRD pattern of $Ca_3Si_2O_7$:$0.02Ce^{3+}$, $0.006Eu^{2+}$ and standard data of $Ca_3Si_2O_7$.

3.2. SEM images

Fig. 2 shows the scanning electron micrographs of the obtained $Ca_3Si_2O_7$:$0.02Ce^{3+}$, $0.006\,Eu^{2+}$ phosphor. As shown in Fig. 2(a), the morphology of synthesized materials demonstrates the irregular particle size distribution ranging from 1 to 20 μm. Fig. 2(b) is the enlarged SEM image from a selected region in Fig. 2(a), and indicates that there are many small crystallites on the surface of large crystallites due to the aggregation effect of particles.

3.3. Optical properties

The excitation and emission spectra of $Ca_3Si_2O_7$:Ce^{3+} and $Ca_3Si_2O_7$:Eu^{2+} are represented in Fig. 3. Under the excitation of n-UV light ($\lambda_{ex}=350$ nm), $Ca_3Si_2O_7$:Ce^{3+} shows an asymmetric blue emission band that extends from 400 to 520 nm. The asymmetric emission band consists of a strong broad band with maximum at 440 nm and a weak band with maximum at 455 nm, which are attributed to the transition of the Ce^{3+} ions from the 5d excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground states, respectively [14]. As shown in Fig. 3(a), the excitation spectrum of $Ca_3Si_2O_7$:Ce^{3+} phosphor displays two bands at 320 nm and 370 nm, the latter excitation intensity is stronger than the former, which is very important for the n-UV LED chip.

Fig. 3(b) shows the emission and excitation spectra of the $Ca_3Si_2O_7$:Eu^{2+} sample. Because Eu^{2+} ion has many excited states, the excitation spectrum is composed of unresolved multiple excitation bands, which are mainly resulted from the transitions from $4f^7$ ground state to $4f^65d^1$ excited states [12]. The phosphor can be efficiently excited by UV light and blue light, which is very advantageous for application in white

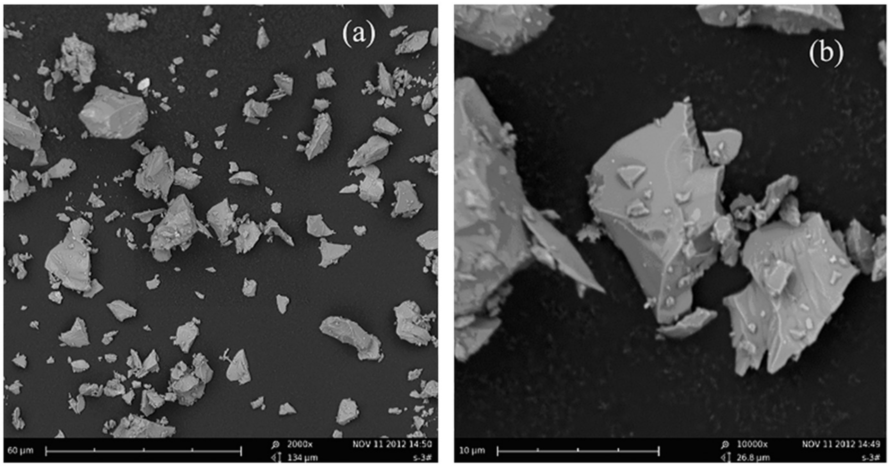

Fig. 2. SEM image (a) and enlarged SEM image (b) of $Ca_3Si_2O_7$:$0.02Ce^{3+}$, $0.006Eu^{2+}$ phosphor.

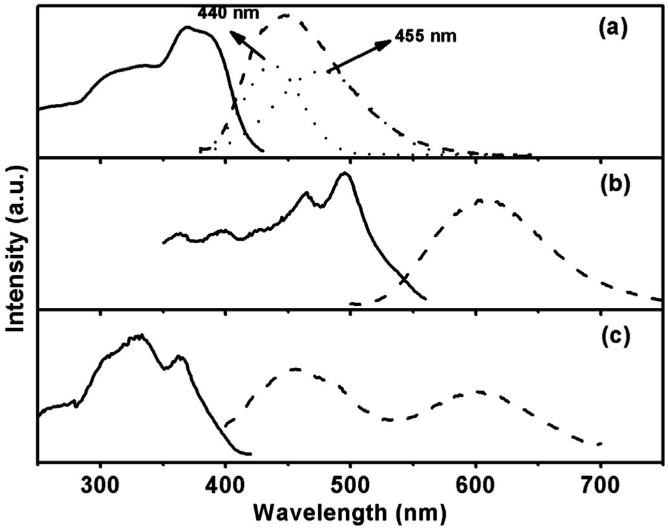

Fig. 3. Excitation (solid curve) and emission (dash curve) spectra of phosphors with composition of $Ca_3Si_2O_7$:Ce^{3+} (a), $Ca_3Si_2O_7$:Eu^{2+} (b), and $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} (c).

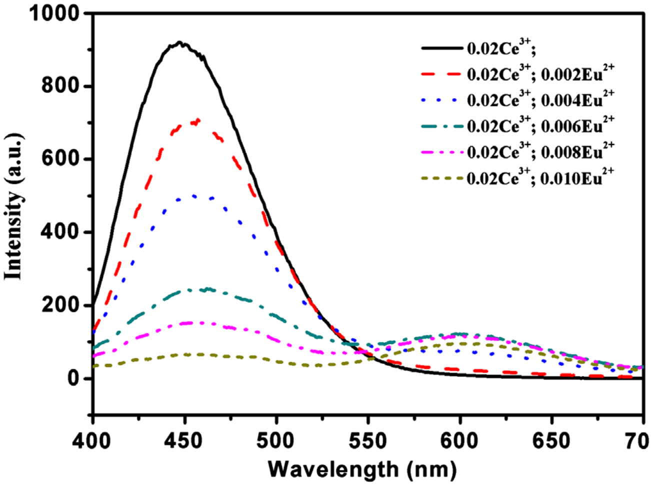

Fig. 4. Emission spectra of $Ca_3Si_2O_7$:$0.02Ce^{3+}$, xEu^{2+} phosphors under 360 nm excitation.

LED. As shown in Fig. 3(b), the $Ca_3Si_2O_7$:Eu^{2+} phosphor shows a broad emission band centered at about 610 nm due to the $4f^65d^1 \rightarrow 4f^7$ allowed transition of Eu^{2+}, which is in agreement with the report of Fu, and not with Yoon and Zhang [11,15,16]. Although Eu^{2+} ions occupy three different crystallographic Ca^{2+} sites, their neighboring environment is very similar, which results in a single symmetric emission band [11]. The strong red emission of $Ca_3Si_2O_7$:Eu^{2+} indicates that it can be used in white LED, and enhances the CRI of white light.

On the base of the excitation spectra of Ce^{3+} or Eu^{2+} ions, $Ca_3Si_2O_7$:Eu^{2+} phosphor has lower absorption in n-UV region than blue region, however, $Ca_3Si_2O_7$:Ce^{3+} phosphor has strong absorption in n-UV region. Moreover, Fig. 3(a) and (b) shows a large overlap between the emission spectrum of Ce^{3+} and the excitation spectrum of Eu^{2+} in $Ca_3Si_2O_7$ host lattice, therefore, it is expected that an efficient energy transfer can take place from Ce^{3+} to Eu^{2+}. Ce^{3+} and Eu^{2+} are doped together into the $Ca_3Si_2O_7$ host lattice, and used as energy donor and acceptor, respectively. Ce^{3+} and Eu^{2+} co-doped sample is expected to show efficient energy transfer and excellent luminescence properties. As shown in Fig. 3(c), the co-doped sample exhibits two obvious emission bands centered at about 450 and 610 nm, which is attributed to the 5d transition of Ce^{3+} and Eu^{2+}, respectively. Comparing Fig. 3(b) and (c), the absorption intensity of co-coped sample is stronger than that of Eu^{2+} single-doped samples in the n-UV region, which proves the occurrence of energy transfer from Ce^{3+} to Eu^{2+} ions.

3.4. *Luminescence properties and energy transfer*

In order to further investigate the energy transfer and luminescence properties, we have synthesized a series of samples with fixed Ce^{3+} concentration and varied Eu^{2+} concentration. Fig. 4 exhibits the emission spectra of $Ca_3Si_2O_7$:$0.02Ce^{3+}$, xEu^{2+} phosphors ($x=0$, 0.002, 0.004, 0.006, 0.008, and 0.010) under 365 nm excitation, which contain blue and red emission bands, centered at 450 nm ($4f^65d^1 \rightarrow 4f^7$ transition of Ce^{3+}) and 610 nm ($4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}), respectively. With the increase of Eu^{2+} concentration, the intensity of the blue emission decreases remarkably, whereas the red emission intensity gradually enhances, and then begins to weaken after reaching a maximum value at $x = 0.006$. The increase and the decrease of the red emission intensity are primarily attributed to the energy transfer and the concentration quenching, respectively.

In order to further confirm the energy transfer between Ce^{3+} and Eu^{2+} in $Ca_3Si_2O_7$ phosphor, the energy transfer efficiency (η_T) can be obtained by Dexter's energy transfer formula of multipolar interaction [17].

$$\eta_T = 1 - \frac{I_s}{I_{so}} \tag{1}$$

where I_{S0} and I_S are the luminescence intensities of the Ce^{3+} sensitizer with and without Eu^{2+} activator, respectively. As shown in Fig. 5(a), with the increase of Eu^{2+} concentration, the energy transfer efficiency increases, whereas the increscent rate of η_T decreases gradually. The η_T can reach 93%, which shows the energy transfer from Ce^{3+} to Eu^{2+} is very important to enhance Eu^{2+} emission intensity. On the basis of Dexter's energy transfer expressions of multipolar interactions, the following relation can be given as [9,18]

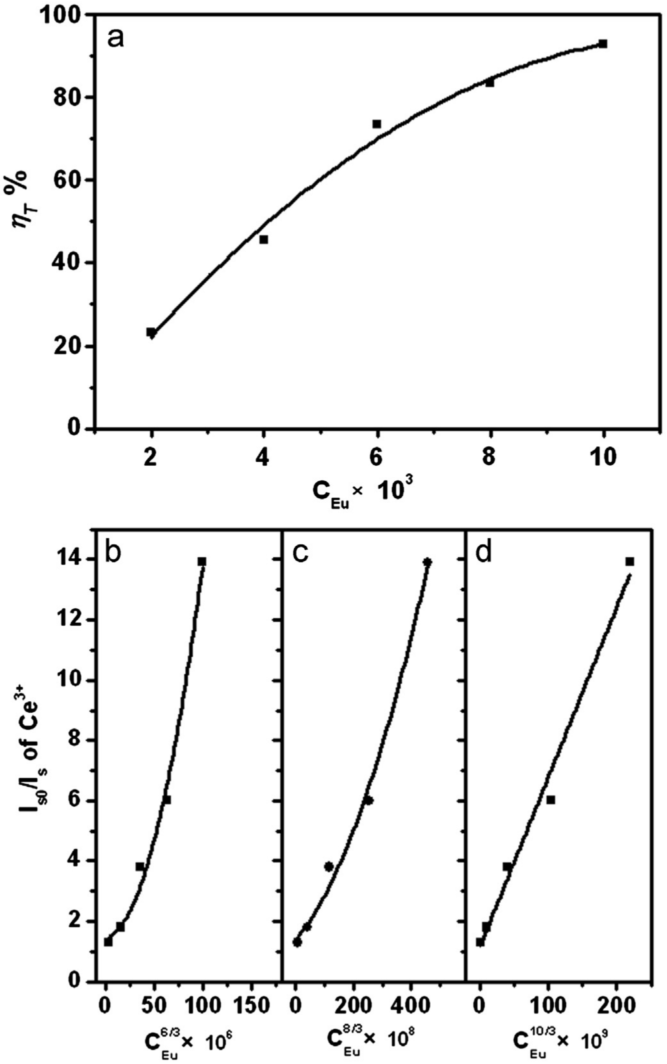

Fig. 5. Dependence of η_T of Ce^{3+} on C (a); I_{so}/I_s of Ce^{3+} on $C^{6/3}$ (b); $C^{8/3}$ (c); and $C^{10/3}$ (d).

$$\ln\left(\frac{I_{so}}{I_s}\right) \propto C \tag{2}$$

$$\frac{I_{so}}{I_s} \propto C^{\alpha/3} \tag{3}$$

where C is the concentration of Eu^{2+}, $\ln(I_{SO}/I_S)$ versus $C^{\alpha/3}$ corresponds to the exchange interaction, and the plots of (I_{SO}/I_S) versus $C^{\alpha/3}$ with $\alpha=6$, 8, and 10 corresponds to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. As shown in Fig. 5(b)–(d), a linear relationship is obtained only when $\alpha = 10$, which implies that the energy transfer from the sensitizer Ce^{3+} to the activator Eu^{2+} follows a quadrupole–quadrupole interaction mechanism. The critical distance (R_c) of energy transfer is estimated by using the concentration quenching method. A rough estimation of R_c can be calculated using the relation given by Blasse [19].

$$R_c \approx 2\left(\frac{3V}{4\pi X_c Z}\right)^{1/3} \tag{4}$$

where V is the unit cell volume, and Z is the number of formula units per unit cell. X_c is the total concentration of Ce^{3+} and Eu^{2+} ions, when the emission intensity of $Ca_3Si_2O_7$:0.02 Ce^{3+}, $x$$Eu^{2+}$ phosphors reaches the maximum. On the basis of structural parameters, $V = 648.127$ Å^3, $Z = 4$, $X_c = 0.026$, R_c is determined to be 22.836 Å.

3.5. CIE

Fig. 6 provides the CIE chromaticity summaries of $Ca_3Si_2O_7$:0.02Ce^{3+}, $x$$Eu^{2+}$ phosphors. With the increase of Eu^{2+} content, the color tone can be tuned from blue to white, and eventually to orange in the visible spectral region. The

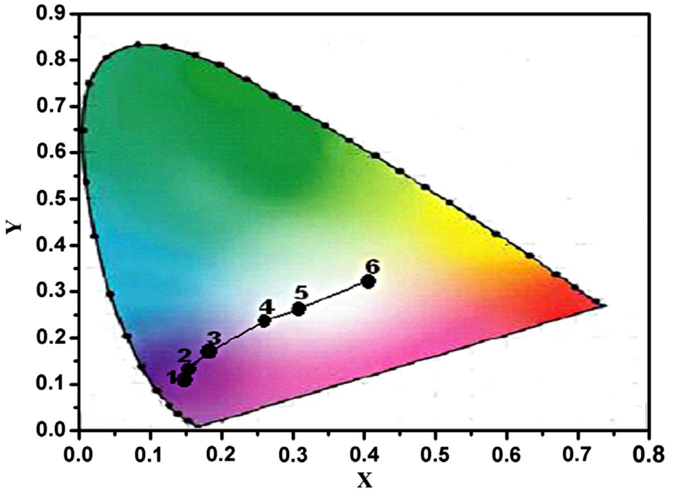

Fig. 6. CIE chromaticity diagram for $Ca_3Si_2O_7$:0.02Ce^{3+}, $x$$Eu^{2+}$ phosphors under 360 nm excitation, (1) $x=0.000$; (2) $x=0.002$; (3) $x=0.004$; (4) $x=0.006$; (5) $x=0.008$; and (6) $x=0.010$.

samples have tunable emission bands, thus, the white light with high CRI can be obtained with varied Eu^{2+} concentration. The results show composition-optimized $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} can be useful for the development of white LEDs with a single-phased phosphor.

4. Conclusions

In this report, we have successfully prepared a single-phased $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} phosphor by high temperature solid-state reaction with H_3BO_3 as the flux. The emission color of the phosphors can be tuned from blue to white, and eventually to orange by adjusting Eu^{2+} concentration due to the different emission bands of Eu^{2+} and Ce^{3+}. The high energy transfer efficiency from Ce^{3+} to Eu^{2+} is discovered in $Ca_3Si_2O_7$ host lattice, and reaches 93% when Eu^{2+} concentration is about 0.01 per molecular. The energy transfer mechanism is demonstrated to be electric quadrupole–quadrupole interaction. Preliminary investigation indicates $Ca_3Si_2O_7$:Ce^{3+}, Eu^{2+} phosphor is a potential single-phased white phosphor for white LEDs with high color rendering index.

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