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White-emission in single-phase $\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}:\text{Ce}^{3+}, \text{Eu}^{2+}, \text{Sm}^{3+}$ phosphor for white-LEDs

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ABSTRACT

To develop new white-light-emitting phosphor, a series of $\text{Ce}^{3+}\text{-Eu}^{2+}\text{-Sm}^{3+}$ doped $\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}$ (BGS) phosphors were prepared by the solid-state reaction method, and their photoluminescence properties were studied. The Ce^{3+} and Eu^{2+} single-doped BGS show broad emission bands around in the region of 350–550 and 420–650 nm, respectively. By co-doping $\text{Ce}^{3+}\text{-Eu}^{2+}$ into BGS, the energy transfer (ET) from Ce^{3+} to Eu^{2+} is inefficient, which could be due to the competitive absorption between the two activator ions. The Sm^{3+} -activated BGS exhibits an orange-red emission in the region of 550–750 nm. To achieve white emission, the $\text{BGS}:0.06\text{Ce}^{3+}, 0.04\text{-Eu}^{2+}, y\text{Sm}^{3+}$ ($0 \leq y \leq 0.18$) phosphors were designed, in which the ET from $\text{Ce}^{3+}/\text{Eu}^{2+}$ to Sm^{3+} was observed. The emission color can be tuned by controlling the Sm^{3+} concentration, and white emission was obtained in the $\text{BGS}:0.06\text{Ce}^{3+}, 0.04\text{Eu}^{2+}, 0.06\text{Sm}^{3+}$ sample. The investigation of thermal luminescence stability for the typical $\text{BGS}:0.06\text{Ce}^{3+}, 0.04\text{Eu}^{2+}, 0.06\text{Sm}^{3+}$ sample reveals that the emission intensities of both Eu^{2+} and Sm^{3+} demonstrate continuous decrease but the Ce^{3+} emission is enhanced gradually with increasing temperature. The corresponding reason has been discussed.

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1. Introduction

Over the past few years, white light-emitting diodes (LEDs) have been paid much attention due to many excellent characteristics, such as high efficiency, long lifetime, reliability, toxicity-free and energy-saving, etc. [1–4]. Generally, white LEDs can be fabricated by modulating the lights from red, green and blue color-emitting LED chips or by combining color-converting phosphors with LEDs (pc-LEDs) [5,6]. Unfortunately, the LEDs made up of red, green and blue LED chips are expensive, and the main problem is that the output light derived from various monochrome LED chips varies with time and temperature. For pc-LEDs, there are three types. A blue-emitting LED (InGaN) coated with a yellow YAG: Ce^{3+} phosphor is the most common one due to a low fabrication cost and high luminous efficiency [6]. However, this kind of LEDs produces a low color-rendering index (CRI, 70–80) and a high correlated color temperature (CCT, ~7750 K) owing to the color deficiency in red region, which is not suitable for applications requiring high CRI properties, such as residential and medical lighting [7,8]. With the remarkable development of ultraviolet (UV) diodes, the combination of a UV chip with three individual red, green and blue phosphors provides a second way to generate white light with excellent CRI value [8–10]. Nevertheless, the blue emission efficiency is low in this system on account of the strong reabsorption of the blue light caused by the red

and green phosphors [7,11]. To overcome this disadvantage, a third way using a single-phase white-light-emitting phosphor that can be excited effectively by UV light has attracted much attention, which also has the merits of color stability and excellent CRI [8,12,13]. As is known, the eventual performance of white LED-based devices strongly depends on the luminescence properties of the phosphors used, so developing new phosphor materials that can be efficiently excited by UV light is urgent at present.

With regard to the rare earth (RE) activators in phosphors for LEDs, the most used ions are Eu^{2+} and Ce^{3+} which show broad excitation and emission originating from the parity allowed transitions between 5d and 4f levels [13,14]. Moreover, their 5d states are out orbital, resulting in the emission is strongly dependent on the host lattice and can be shifted from UV to the red region. The Sm^{3+} ion could give orange or red emission with the predominant emission peaks located at about 600 nm [15,16]. However, the luminous efficiency of Sm^{3+} is weak due to the line 4f–4f transition peaks. Thus, a sensitizer with broad absorption band such as Eu^{2+} or Ce^{3+} is usually needed to improve its emission intensity. In addition to the luminescent ions, selecting suitable host material is another important step to obtain desirable phosphor materials. It has been known that silicates are of interest host materials for their various crystal structures and high physical-chemical stability. Recently, Wiczonek et al. reported a new silicate $\text{Ba}_2\text{Gd}_2\text{Si}_4\text{O}_{13}$ (BGS) which contains finite zigzag-shaped Si_4O_{13} chains and Gd_2O_{12} dimers [17]. Later, the $\text{Eu}^{2+}/\text{Eu}^{3+}/\text{Ce}^{3+}$ single-doped BGS phosphors excited by ultraviolet (UV) light were synthesized and studied [18–21];

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Zhang et al. reported the luminescence properties of the $\text{Eu}^{3+}/\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Dy}^{3+}/\text{Sm}^{3+}$ activated BGS phosphors under vacuum ultraviolet (VUV) excitation [22]. To the best of our knowledge, the Ce^{3+} - Eu^{2+} - Sm^{3+} trioped BGS phosphors for white emission in LED application haven't been investigated at present. In this work, the spectral characteristics and energy transfer (ET) of $\text{BGS}:\text{Ce}^{3+}, \text{Eu}^{2+}, \text{Sm}^{3+}$ were reported.

2. Experimental

The powder samples of $\text{Ba}_2 - x\text{Gd}_{1.94} - y\text{Si}_4\text{O}_{13} : 0.06\text{Ce}^{3+}, x\text{Eu}^{2+}, y\text{Sm}^{3+}$ ($\text{BGS}:0.06\text{Ce}^{3+}, x\text{Eu}^{2+}, y\text{Sm}^{3+}$, $0 \leq x \leq 0.08$, $0 \leq y \leq 0.18$) and $\text{Ba}_{1.88}\text{Gd}_2\text{Si}_4\text{O}_{13} : 0.06\text{Ce}^{3+}, 0.06\text{K}^+$ ($\text{B}_{1.88}\text{GS}:0.06\text{Ce}^{3+}, 0.06\text{K}^+$) were prepared by the solid-state reaction method. The starting materials included BaCO_3 (99%), SiO_2 (99%), Gd_2O_3 (99.99%), Eu_2O_3 (99.99%), Sm_2O_3 (99.99%), CeO_2 (99.99%), K_2CO_3 (99%) and Li_2CO_3 (99%). Stoichiometric amounts of the starting materials were thoroughly mixed and ground together in an agate mortar. 2 wt% Li_2CO_3 was added as the flux. K_2CO_3 was used as charge compensator when synthesized the $\text{B}_{1.88}\text{GS}:0.06\text{Ce}^{3+}, 0.06\text{K}^+$ sample. The reactant mixture was calcined at 1020 °C for 4 h in a reduction atmosphere (95% N_2 -5% H_2).

The phase purity was determined by using an ARL X'TRA powder X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV and 35 mA, the powder sample was packaged in a plastic sample cell, which was then placed on the fixed sample holder. The photoluminescence (PL) spectra and decay curves were recorded on an EI-FS5 fluorescence spectrophotometer. The spectral resolution and wavelength accuracy are 0.1 and ± 0.5 nm, respectively. The excitation and emission spectra were corrected by using the standard light source of the halogen tungsten lamp and deuterium lamp. The time resolution for recording decay curves was 95 ps. The temperature-dependent measurement was also carried out by the EI-FS5 fluorescence spectrophotometer, and the samples were mounted on a heating device, the temperature of which could be changed from room temperature to 573 K with the step of 0.1 K. The Commission International de l'Eclairage (CIE) chromaticity coordinates were calculated by the emission spectra using the 1931 CIE system via the Edinburgh FS5 Instrument.

3. Results and Discussion

Fig. 1(a) presents the XRD patterns of the $\text{BGS}:0.06\text{Ce}^{3+}, x\text{Eu}^{2+}, -y\text{Sm}^{3+}$ ($0 \leq x \leq 0.08$, $0 \leq y \leq 0.24$) phosphors. It can be found the diffraction peaks of these samples could be well indexed to the calculated pattern of BGS by using the data in Ref. [17]. In view of the effective

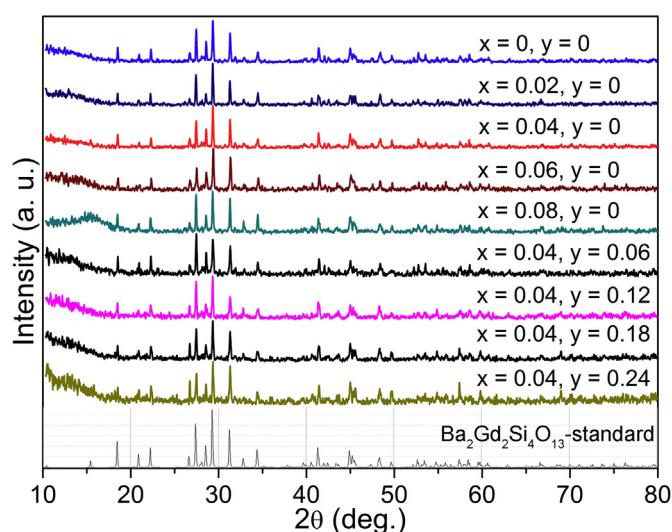


Fig. 1. XRD patterns of $\text{BGS}:0.06\text{Ce}^{3+}, x\text{Eu}^{2+}, y\text{Sm}^{3+}$ ($0 \leq x \leq 0.08$, $0 \leq y \leq 0.24$).

radii and valences, the Ce^{3+} and Sm^{3+} are expected to occupy the Gd^{3+} sites and the Eu^{2+} is suggested to replace the Ba^{2+} preferentially. The XRD patterns indicate the introduction of Ce^{3+} , Eu^{2+} and Sm^{3+} doesn't cause obvious impurity phase and all the as-prepared samples are single-phase. On the other hand, when introducing $\text{Ce}^{3+}/\text{Eu}^{2+}/\text{Sm}^{3+}$, the crystal-field around cation ions will vary owing to their different ionic radii, which would further affect the spectra since the 5d orbitals of Ce^{3+} and Eu^{2+} existing in the outer shell are more sensitive to the environmental condition compared with 4f orbitals [23].

According to Refs [19,20], the optimal Eu^{2+} and Ce^{3+} concentrations were determined to be 2 and 3 mol%, respectively. Fig. 2(a) shows the excitation ($\lambda_{\text{em}} = 513$ nm) and emission ($\lambda_{\text{ex}} = 360$ nm) spectra of the typical $\text{BGS}:0.04\text{Eu}^{2+}$ phosphor. It can be seen that the excitation spectrum covers a broad wavelength region from 240 to 430 nm, which could be attributed to the $4f^7-4f^65d^1$ transition of Eu^{2+} [20]. Upon 360 nm excitation, the $4f^65d^1-4f^7$ transition band of Eu^{2+} is located in the visible range of 420–650 nm peaking at 513 nm. Besides, some weak line emission peaks are observed mainly at 612 and 622 nm. These line emission peaks could be assigned to the $^5\text{D}_0-^7\text{F}_2$ transition of Eu^{3+} , which reveals that the Eu^{3+} was not reduced to Eu^{2+} absolutely. To learn the emitting light color of this sample, the CIE chromaticity coordinates were calculated to be (0.265, 0.500) from the emission spectra. Thus, a green emission has been obtained in the Eu^{2+} -activated BGS, as shown in the CIE chromaticity diagram in Fig. 3 (see Point 1). Fig. 2(b) shows the excitation ($\lambda_{\text{em}} = 398$ nm) and emission ($\lambda_{\text{ex}} = 333$ nm) spectra of the typical $\text{BGS}:0.06\text{Ce}^{3+}$ sample. Three main excitation bands centered at 266, 311 and 333 nm have been observed in the excitation spectrum, which could be ascribed to the $4f^1-4f^0d^1$ transition of Ce^{3+} [24]. The Ce^{3+} $4f^0d^1-4f^1$ emission is found in the range from 350 to 550 nm. The CIE chromaticity coordinates were calculated to be (0.163, 0.054), indicating a blue-purple emission in Ce^{3+} -activated BGS phosphor (see Point 2 in Fig. 3).

To study the ET characteristics between Ce^{3+} and Eu^{2+} in the Ce^{3+} - Eu^{2+} codoped BGS phosphors, the emission spectra of the $\text{BGS}:0.06\text{Ce}^{3+}, x\text{Eu}^{2+}$ ($0 \leq x \leq 0.08$) and $\text{BGS}:0.02\text{Eu}^{2+}$ samples under 333 nm excitation are shown in Fig. 4(a). It can be seen the emission intensity of Ce^{3+} exhibits a continuous decrease with increasing Eu^{2+} concentration. The Eu^{2+} emission is very weak. From the enlarged emission spectra, the emission intensity of Eu^{2+} is also found to decrease gradually when increasing the Eu^{2+} concentration. More importantly, the Eu^{2+} emission in the Ce^{3+} - Eu^{2+} codoped samples has been largely weakened compared with that in the Eu^{2+} -single-doped BGS.

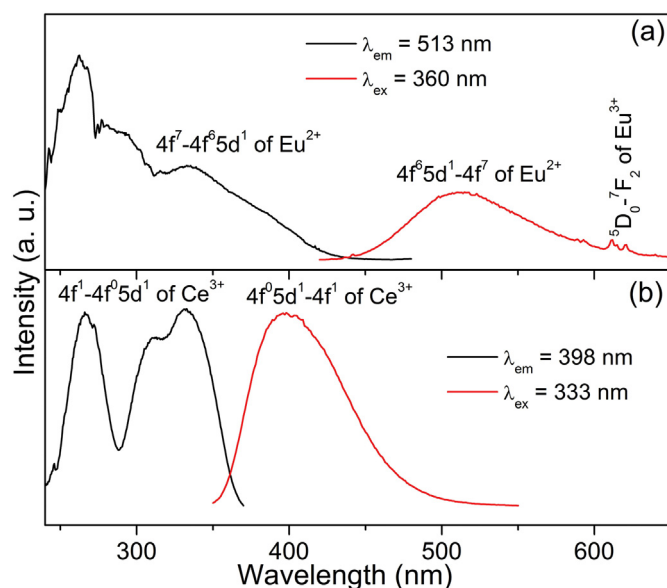


Fig. 2. Excitation and emission spectra of (a) $\text{BGS}:0.04\text{Eu}^{2+}$ and (b) $\text{BGS}:0.06\text{Ce}^{3+}$.

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