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Near UV based LED fabricated with $K_2Ba_3Si_8O_{20}$:Eu^{2+} and energy transfer between Ce^{3+} and Eu^{2+}

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ABSTRACT

$K_2Ba_3Si_8O_{20}$:Eu^{2+} as a new green-emitting phosphor was prepared and studied in this article. This material showed powerful absorption in near ultraviolet-visible regions from 350 to 450 and its green-emitting band peaked at 502 nm. Its photoluminescence emitting intensity affected by concentrations of $K_2Ba_3Si_8O_{20}$:Ce^{3+} and $K_2Ba_3Si_8O_{20}$:Eu^{2+} was also studied and consequently verified to be a dipole–dipole interaction. Effective energy transfer was observed in Ce^{3+},Eu^{2+} co-doped $K_2Ba_3Si_8O_{20}$ phosphor, and the transfer efficiency was also obtained from the decay lifetime. The $K_2Ba_3Si_8O_{20}$:Eu^{2+} phosphor combined with a 380 nm near-UV chip was demonstrated to produce a diode which emitted green light. This article indicates that the phosphor prepared in this work could be used in manufacturing of white light-emitting diodes.

1. Introduction

Phosphor-conversion based diodes which emit white light have two main types, one of which is a blue chip combined with a yellow-emission phosphor [1]. White light of this type, however, shows a high thermal quenching and a low color rendition due to deficient colors in red and blue-green regions [2–4]. For this reason, near- ultraviolet and ultraviolet LED chips were proposed for general illumination to excite the blends of red, green, and blue emitting phosphors [5–7], which could produce better CRI (Color Rendition Index) than the technique of blue with YAG:Ce^{3+}. In addition, green LED can serve as traffic signals with specific requirements, which can emit green lights in a main wave length of approximately 505 nm [8]. In this regard, many efforts were made to develop new green phosphors. The main WLED green phosphors are usually grouped into nitride and oxynitride respectively represented by SiAlON:$Eu^{2+}$and $Si_2Si_2O_2N_2$:Eu^{2+} [9,10]. For the former, it has to be synthesized in critical conditions, such as high temperance and high pressures, which affect its application in white LED. On the other hand, rare earth doped with alkaline and alkaline-earth silicates have drawn attentions because of their good structural diversity, good chemical and thermal stability, and relatively easy preparation [11–13].

As is well-known, Eu^{2+} and Ce^{3+} ions could be used as important activators in luminescent materials based on the 5d-4f electric dipole transitions, because the emitting of the two ions are very special and their emitting spectrums are wide, which ensures high color rendering and short decay time and consequently avoids saturation [14–19]. Furthermore, they have wide excitation/emission bands and good spectral features that fit well with LED characteristics. Especially, Eu^{2+} activated phosphors which emit green bands have been widely adopted as green light in many hosts, such as $Sr_8ZnLu(PO_4)_7$: Eu^{2+} [20], $Na_2Ba_6(Si_2O_7)(SiO_4)_2$: Eu^{2+} [21], $Ca_{2\text{-}x/2}(Si_{1\text{-}x}P_x)O4$: Eu^{2+} [22], $Ca_2MgSi_2O_{7\text{-}x}N_x$: Eu^{2+} [23], $Ba_5Si_2O_6Cl_6$:Eu^{2+} [24], $BaZrSi_3O_9$:Eu^{2+} [25], $Ba_3Ca_2(PO_4)_3F$: Eu^{2+} [26].

In this work, a strong green emitting $K_2Ba_3Si_8O_{20}$:Eu^{2+} with low calcining temperatures was synthesized. This phosphor was verified suited to excite near UV light. Its luminescent properties and emitting intensity affected by Eu^{2+} concentrations are studied. In addition, because of the sensitizing use of Ce^{3+} ions, energy-transfer between Ce^{3+} and Eu^{2+} was discussed. We especially focus on green LED fabricated with synthesized phosphors on 380 nm near-UV chips to verify their applicability.

2. Experimental

The $K_2Ba_3Si_8O_{20}$:xCe^{3+},yEu^{2+} (KBSO: xCe^{3+},yEu^{2+}) phosphors were synthesized by a high-temperature solid-state reaction. The starting materials, $BaCO_3$ (A.R. (Analytical Reagent)), K_2CO_3 (A.R. (Analytical Reagent)), SiO_2(A.R.), CeO_2 (99.99%) and Eu_2O_3(99.99%) were employed by an agate mortar and placed in a cruciblewith a lid.. The $BaCO_3$, SiO_2 and K_2CO_3 of reagent grade, were mixed together with a mole ratio of $BaCO_3$, SiO_2, and K_2CO_3 = 3:8:1:1. The well-mixed

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reactants were placed in a crucible closed with a lid. The reactants were calcined at 950 °C in 10% H_2/90% N_2 for 4 h. The prepared phosphors were cooled to room temperature and then reground for further measurements.

The compositions were checked for phase formation by powder X-ray diffraction (XRD) data were collected using Cu Kα radiation (λ = 1.54056 Å) on a Bruker D8 Advance diffractometer equipped with a linear position-sensitive detector (PSD-50 m, M. Braun), operating at 40 kV and 40 mA with a step size of 0.02° (2θ). The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded on powder samples using a Hitachi F7000 spectrometer equipped with a 150 W xenon lamp under a working voltage of 700 V. The luminescence decay curve was obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using a tunable laser (pulse width = 4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO). All the measurements were performed at room temperature.

3. Results and discussion

XRD patterns of the Ce^{3+} and Eu^{2+} activated KBSO samples are shown in Fig. 1, which indicates these samples can be exactly assigned to the pure KBSO phase even though the Ce^{3+}, Eu^{2+} ions are introduced in a host lattice. Since there are neither other phases nor impurities, meaning the materials prepared in this paper can be concluded as single phase and no significant changes occur in the doped Ce^{3+} or Eu^{2+} ions.

PLE and PL spectra of KBSO: Ce^{3+} and KBSO: Eu^{2+} is shown in Fig. 2a. The PLE spectrum of Ce^{3+} monitored at 400 displays an excitation band at 295 nm, which comes from absorption of Ce^{3+} ion in its 4*f*→5*d* transition. The PL spectrum shows strong broadband emissions taking 390 nm as the center, owing to its 5d-$4f^1$ transition of the KBSO:Ce^{3+}. Fig. 2a also shows intensive absorptions ranging the length 250 to 450 nm, which comes from Eu^{2+} transitions enabled by 4f–5d electronic dipole. The conspicuous overlapping in Fig. 2a shows that energy transfers among the sensitizer Ce^{3+} and the activator Eu^{2+} occur in the KBSO host. The very broad excitation spectrum indicated that the phosphor is useful as a good and environment friendly material in manufacturing of white LED. The Ce^{3+} concentration is varied in KBSO for the examination of its effect. Emission spectra of the as-obtained KBSO:xCe^{3+} (x = 0.02, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14) materials are shown in Fig. 2b, and the relationship of the peak emitting intensity with the Ce^{3+} doping content are indicated by the inset. It clearly shows that at 390 nm the Ce^{3+} firstly increases its emitting intensity with its concentration until the point x = 0.06, when it begins to decrease the intensity, owing to the quenching effect of the concentration. The emitting spectra of KBSO:yEu^{2+} phosphor with doped (y = 0.04, 0.08, 0.12, 0.16, 0.18, 0.20, 0.24 and 0.28) are presented in Fig. 2c, where we could find intensive green emissions, with the maximum occurred at about x = 0.16, after which the intensity decreases owing to energy migration and the consequent concentration quenching. Otherwise, this quenching is basically due to non-radiative energy transfer among Ce^{3+}/Eu^{2+}, as we deduced according to the Dexter theory. As reported by Uitert, the interaction mechanism between Ce^{3+}/Eu^{2+} ions is determined using this formula [27,28]

$$\frac{I}{x} = K\left[1+\beta(x)\frac{Q}{3}\right]^{-1} \tag{1}$$

where I is emitting intensity, x is content of Ce^{3+} or Eu^{2+}, K and β are constants. According to formula (1), Q *is* 6, 8 and 10 respectively for interaction of d–d (dipole–dipole), d–q (dipole–quadrupole), and q–q (quadrupole–quadrupole). For Q value of emission center, we plot the dependence of log (I/x) on log (x) (refer Fig. 2d). In this plot, the straight line has a slope of Q/3. The values of the slope for KBSO:Ce^{3+} and KBSO:Eu^{2+} are 1.883 and 1.652 respectively. Meanwhile the value of Q was determined at 6 roughly, which indicates that the interaction mechanism in KBSO:Ce^{3+} and KBSO:Eu^{2+} phosphors take a key role by dipole-dipole interaction.

Ce^{3+} emission and Eu^{2+}excitation band was compared (in Fig. 2) and revealed a large spectral overlapping between 350 and 400 nm, from which we could expect energy to be transferred in resonance-type from the sensitizer Ce^{3+} to the activator Eu^{2+}. Many phosphors of codoped Ce^{3+} and Eu^{2+}, therefore, have been studied and prepared, such as $Ca_8La_2(PO_4)_6O_2$:Ce^{3+},Eu^{2+}, $Ca_{1.65}Sr_{0.35}SiO_4$: Ce^{3+}/Li^+, Eu^{2+}, $NaMg_4(PO_4)_3$:Ce^{3+},Eu^{2+}, $Sr_3Gd(PO_4)_3$:Ce^{3+},Eu^{2+}, and $Ca_4(PO_4)_2O$:Ce^{3+},Eu^{2+} [29–33]. The current work was to study energy transfer between Ce^{3+} and Eu^{2+}, and therefore it fixed the Eu^{2+} ions concentration and changed the Ce^{3+}concentration systematically. Fig. 3a are the PLE spectra of phosphors of KBSO:0.04Ce^{3+} and KBSO:xCe^{3+},0.1Eu^{2+} at different x (x = 0, 0.01, 0.02 and 0.03). It shows that Eu^{2+} ions in KBSO:xCe^{3+},0.1Eu^{2+} and KBSO:0.04 Ce^{3+} take a similar shape of PLE band, compared to PLE spectrum in 275–320 nm for KBSO:0.1Eu^{2+}. Fig. 3b displays PL spectra of KBSO:xCe^{3+},0.1Eu^{2+} excited at 300 nm. The green emissions (503 nm) caused by Eu^{2+} emissions are enhanced in

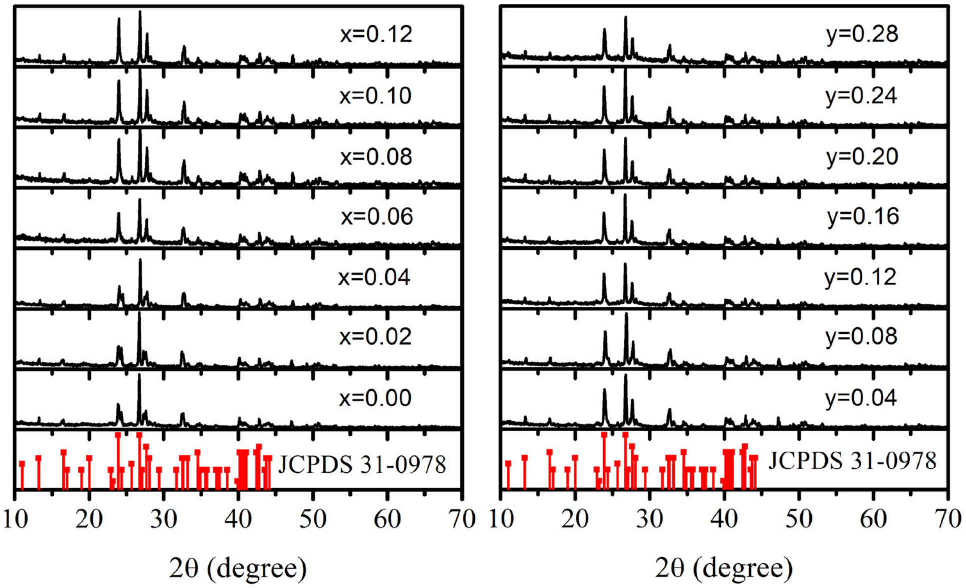

Fig. 1. XRD patterns of as-prepared KBSO:xCe^{3+} and KBSO:yEu^{2+}. The standard pattern for $K_2Ba_3Si_8O_{20}$ (JCPDS 31- 0978) is shown as a reference.