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Cyan-emitting $BaZrSi_3O_9:Eu^{2+}$ phosphors for near-UV based white light-emitting diodes

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ABSTRACT

A series of Eu^{2+} ions doped $BaZrSi_3O_9$ phosphors were synthesized by a solvothermal reaction method. The X-ray diffraction patterns of $BaZrSi_3O_9:Eu^{2+}$ phosphors confirmed their hexagonal structure after the samples were sintered above 1300 °C. The photoluminescence properties of $BaZrSi_3O_9:Eu^{2+}$ phosphors were explored by measuring the excitation and emission spectra, and decay curves. The excitation spectra of $BaZrSi_3O_9:Eu^{2+}$ phosphors consist of broad bands in the ultraviolet (UV) region due to $4f^8 \rightarrow 4f^7 5d^1$ transition of Eu^{2+} ions. The sintering temperature and Eu^{2+} ion concentration of $BaZrSi_3O_9:Eu^{2+}$ phosphors were optimized based on the dominant cyan emission intensity under the near-UV excitation. The optimum doping concentration of Eu^{2+} ions was 3 mol% and the critical distance was calculated to be 23.245 Å. These luminescent powders are expected to be a potential candidate for solid-state lighting based white light-emitting diodes and optical display systems.

1. Introduction

Recently, light-emitting diode (LED) chips have been developed across the ultraviolet (UV), visible and infrared wavelength ranges, and their application field has been extended from interior and exterior to display parts. White LEDs (WLEDs) by the combination of a LED chip and different kinds of phosphors have attracted much attention because of their significant advantages for general illumination applications such as lower energy consumption, high reliability, environmentally-friendly nature, small size, long working lifetime and high efficiency [1–5]. Nowadays, most of the commercial WLEDs are being produced by the combination of a blue LED chip and yellow emitting $Y_3Al_5O_{12}:Ce^{3+}$ phosphors [5–7]. Unfortunately, $Y_3Al_5O_{12}:Ce^{3+}$ phosphors-based WLEDs possess high thermal quenching and low color rendering index owing to the lack of the red component. To solve this problem, mainly two types of approaches have been developed: one is UV LED chip combined with red, green and blue phosphors and the other is UV LED chip combined with cyan and red phosphors [6]. For display applications, the introduction of a cyan emitting phosphor could enlarge the display color gamut, so the images of the device may be more colorful and natural because the display characteristics of field-emission displays strongly depend on the emission color of phosphors [7–9].

Eu^{2+} ions with $4f^7$ electronic configuration have potential advantages in optical applications by being utilized in the form of phosphor, laser, or scintillating materials [10]. In literature, Eu^{2+} ions have been explored as a dopant in cyan-emitting phosphors, such as $Ca_3(PO_4)_2:Eu^{2+}$ [7], $Sr_8(Si_4O_{12})Cl_8:Eu^{2+}$ [9], $Sr_6BP_5O_{20}:Eu^{2+}$ [11], $LiBaBO_3:Eu^{2+}$ [12], $BaZrSi_3O_9:Eu^{2+}$ [13] and $BaSi_7N_{10}:Eu^{2+}$ [14]. However, it has become quite clear that the $BaZrSi_3O_9:Eu^{2+}$ phosphors by a solvothermal process have not been reported so far.

Herein, we reported a synthesis of Eu^{2+} ions doped $BaZrSi_3O_9$ phosphors by a solvothermal reaction method. The structural properties were investigated by the X-ray diffraction (XRD) patterns. The optical properties of these phosphors were examined in details by the measurements of photoluminescence (PL) excitation spectra, PL emission spectra and decay curves.

2. Experimental

Eu^{2+} ions doped $BaZrSi_3O_9$ phosphors with different dopant concentrations were prepared by a solvothermal reaction method by taking the stoichiometric amounts in 5 mol% of barium oxide (BaO, 97%, Aldrich), zirconium butoxide ($Zr(OC_4H_9)_4$, 80 wt% in butanol, Aldrich), tetraethyl othosilicate ($Si(OC_2H_5)_4$, TEOS, 98%,

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Table 1
Detailed amounts of starting materials.

$Ba_{(1-x)}ZrSi_3O_9{:}_xEu^{2+}$	Amount (mg)					
	$0Eu^{2+}$	$1Eu^{2+}$	$2Eu^{2+}$	$3Eu^{2+}$	$4Eu^{2+}$	$5Eu^{2+}$
BaO	0.948	0.939	0.929	0.920	0.910	0.901
$Eu(NO_3)_3$	0	0.029	0.058	0.087	0.116	0.144
TEOS	3.826					
$Zr(OC_4H_9)_4$	2.878					

Aldrich), europium nitrate pentahydrate ($Eu(NO_3)_3\cdot 5H_2O$, 99.9%, Aldrich) and detailed amounts of starting materials were presented on Table 1. For the preparation of $BaZrSi_3O_9$:Eu^{2+}phosphors via the solvothermal process, two solutions were prepared separately. Solution I was prepared by taking isopropanol (200 ml) and 1 mol $Zr(OC_4H_9)_4$ in one beaker and solution II with (1−x) mol BaO, x mol $Eu(NO_3)_3$, 3 mol TEOS and methanol (400 ml) were made in another beaker. Two solutions were stirred thoroughly under continuous magnetic stirring for 1 h. After that, the solution I was added dropwise to the solution II and then NH_4OH added into the blended solution for adjusting pH 9 and a milky white colloidal solution immediately formed. Finally, the mixed solution was transferred into a Teflon liner (1 L volume and 60% filling capacity) and was placed in a stainless steel autoclave. It was heated to 230 °C at a rate of 2/min and kept at that temperature for 5 h with magnetic stirring. After cooling gradually to room temperature, the precipite was separated by a centrifugal separator with 3000 rpm for 5 min and then dried at 70 °C in an oven. The dried powders were sintered at different temperatures from 1000 to 1400 °C. A series of Eu^{2+}ions doped $BaZrSi_3O_9$ phosphors were prepared by repeating the above synthesis method.

The structure of $BaZrSi_3O_9$:Eu^{2+}phosphors was analyzed with the powder X-ray diffraction recording on X'PERT PRO X-ray diffractometer with a CuKα = 1.5406 Å at 40 kV of beam voltage and 30 mA of beam current. The luminescence properties were measured at room temperature by using a luminescence spectrophotometer (Photon Technology International (PTI)) with a 60 W xenon arc lamp. The luminescence decay curves were measured using the third harmonic (355 nm) of a pulsed Nd:YAG laser.

3. Results and discussion

Fig. 1 show the comparative XRD patterns of $BaZrSi_3O_9$:Eu^{2+}phosphors at different sintering temperatures from 1000 to 1400 °C. The phosphors were found to be amorphous until the precipitate powders were sintered at 1000 °C. From 1100 °C, different phase developments were observed such as $BaZrO_3$, ZrO_2, $Ba_2Zr_2Si_3O_{12}$ and $BaZrSi_3O_9$. At 1100 °C, the main phase is $BaZrSi_3O_9$ with the presence of $BaZrO_3$, ZrO_2 and $Ba_2Zr_2Si_3O_{12}$ impurity peaks. By increasing the sintering temperature, the $BaZrSi_3O_9$ peaks were increased and the other peaks were decreased. Finally, at 1300 °C, all secondary peaks disappeared and pure $BaZrSi_3O_9$ phase was observed. It is well known that the pure phase is beneficial for getting the better luminescence properties of phosphors. The diffraction peaks are in well agreement with standard JCPDS card [PDF(25-1467)] with space group *P*-6*c*2. Typically, the crystallite size can be estimated by using the Scherrer's equation of $D_{hkl} = k\lambda/\beta\cos\theta$, where D is the average grain size, k (0.9) is a shape factor, λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum and θ is the diffraction angle of an observed peak, respectively. The strongest diffraction peaks are used to calculate the crystallite size of $BaZrSi_3O_9$:Eu^{2+}phosphors, sintered at 1300 °C, which yield the values of about 52 nm.

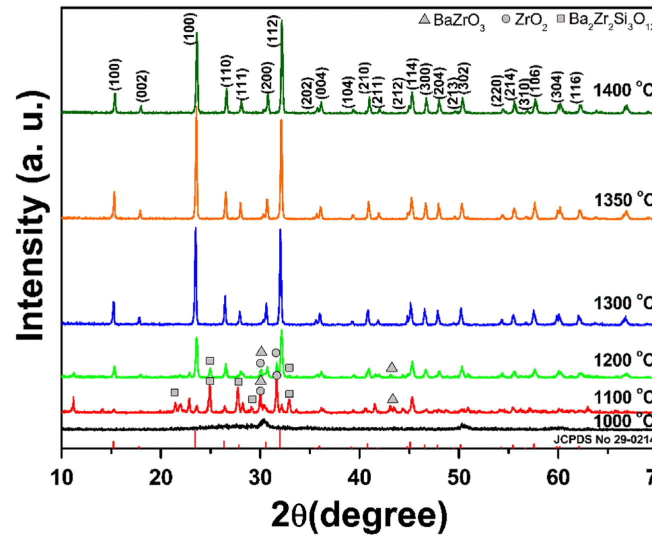

Fig. 1. X-ray diffraction patterns of the $BaZrSi_3O_9$:Eu^{2+}phosphors as a function of sintering temperature.

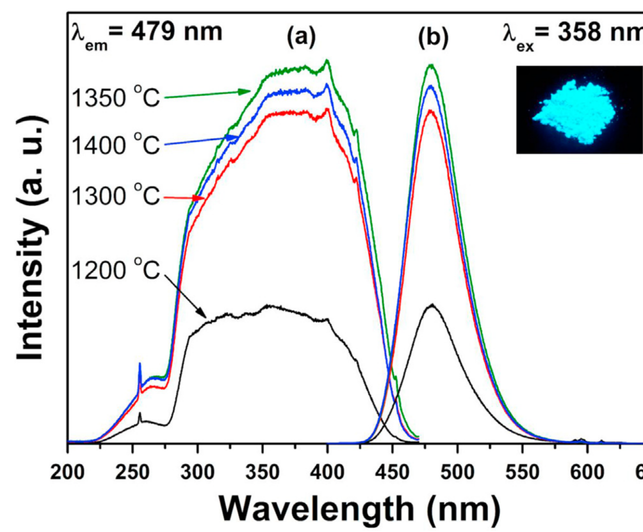

Fig. 2. PL (a) excitation and (b) emission spectra of the $BaZrSi_3O_9$:Eu^{2+}phosphors at different sintering temperatures (inset shows the digital photograph of $BaZrSi_3O_9$:Eu^{2+}phosphors sintered at 1350 °C under an UV irradiation).

The PL excitation and emission spectra of 3 mol% Eu^{2+}ions doped $BaZrSi_3O_9$ phosphors sintered between the temperatures 1200 and 1400 °C are shown in Fig. 2. The excitation spectra of the $BaZrSi_3O_9$:Eu^{2+}phosphors monitored at an emission wavelength of 479 nm revealed an intense and broad band corresponding to the Eu^{2+}ions in the UV and visible regions from 275 to 470 nm with the band maxima at 358 nm that is associated with the $4f^7 \rightarrow 4f^6 5d^1$ electronic transition. This kind of broadband excitation is necessary for the development of near-UV LED chips-based WLEDs. The observed emission spectra by exciting at 394 nm is attributed to the $4f^6 5d^1 \rightarrow 4f^7 5d^{\circ}$ transition of the Eu^{2+}ions incorporated into the $BaZrSi_3O_9$ host lattice. When the sintering temperature increased from 1200 to 1350 °C, the Eu^{2+}integrated emission intensities also increased due to the increased crystallinity of the $BaZrSi_3O_9$ phosphors. When the sintering temperature increased above 1350 °C, however, the emission intensity decreased.

Fig. 3(a) shows the excitation spectra of $BaZrSi_3O_9$:Eu^{2+}phosphors as a function of Eu^{2+}ion concentration by monitoring the emission wavelength of 479 nm. The excitation spectra