



Photoluminescence of BaZrSi₃O₉:Bi³⁺ as a yellow emitting phosphor for White LEDs



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ARTICLE INFO

Article history:

Received 25 February 2016
Received in revised form 6 June 2016
Accepted 11 June 2016
Available online 14 June 2016

Keywords:

Optical materials
Luminescence
Optical properties
X-ray diffraction
Phosphors

ABSTRACT

A yellow-emitting phosphor, BaZrSi₃O₉:Bi³⁺, was synthesized in air via solid state reaction method. Luminescence properties of this phosphor were examined by steady-state and time-resolved as well as temperature-dependent luminescence spectra. The obtained BaZrSi₃O₉:Bi³⁺ sample shows strong absorption in 300–400 nm, and gives bright and broad yellow emission centered at 560 nm upon 350 nm excitation. The broad emission is originated from ³P₁ → ¹S₀ transition of Bi³⁺, which has a lifetime around ~1 μs in BaZrSi₃O₉. Upon heating in the temperature range from room temperature to 250 °C, accompanied by the emission intensity decreases (emission intensity at 150 °C retains 76% its initial intensity at room temperature), the emission of Bi³⁺ in BaZrSi₃O₉ is blue-shifted, which is ascribed to the thermally active phonon-assisted tunneling from the lower energy to the higher energy emission band in the excited states of Bi³⁺.

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1. Introduction

In recent years, owing to their outstanding merits such as environmentally friendly, long operating time, and lower power consumption, white light-emitting diodes (WLEDs) have gained much attention as a new lighting source to replace traditional incandescent lamps [1–4]. Conventional white LED is obtained through a blue LED chip coated with a yellow phosphor YAG:Ce³⁺ [5,6]. However, the white light based on such technique exhibits a low color-rendering index ($R_a \approx 70$ to 80) and a high color temperature ($T_c = 7756$ K) due to red components deficiency in the obtained emission spectrum [7–10]. In order to overcome these drawbacks, WLEDs fabricated by a combination of *n*-UV/UV LED chip with RGB phosphors have been proposed [11]. Especially, the WLEDs obtained by a *n*-UV LED chip combined with a blend of yellow-emitting and blue-emitting phosphors have exhibited favorable properties, including tunable CIE chromaticity coordinates and excellent R_a values [12]. Therefore, it is highly demanded to explore new *n*-UV excitable yellow/blue-emitting phosphors

Recently, the luminescence properties of the Bi³⁺ ion in some host (*ns*² electronic configuration) have been reported, including Y₃Al₅O₁₂:Bi³⁺ [13], (Y,Gd)₃(Al,Ga)₅O₁₂:Bi³⁺ [14], and LnVO₄:Bi³⁺ (Ln = La, Gd and Y) [15]. From which it can be seen that Bi³⁺ can give a variable emission depending on the different hosts. To the best of our knowledge, alkaline-earth and zirconium based silicates are considered to be important owing to their outstanding optical properties coupled with photo-thermal stability and low thermal conductivity [17]. In this work, with an aim to explore new phosphors for white LEDs, we studied the luminescent property of Bi³⁺ in a silicate BaZrSi₃O₉, which was proved to be a good candidate of phosphor host.

2. Experimental

2.1. Sample preparation

Samples of BaZrSi₃O₉:xBi³⁺ (0.5% ≤ *x* ≤ 10%) were synthesized by a solid-state reaction method in air. Stoichiometric amounts of SiO₂ (99.5%, Aldrich), BaCO₃ (99.9%, Aldrich), Zr(NO₃)₄·5H₂O (AR) and Bi₂O₃ (99.99%, Sinopharm Chemical Reagent Co.,Ltd.) were thoroughly grinding in an agate mortar with ethanol serve as the dispersing medium. The obtained powder was then preheated at 800 °C for 2 h and calcined at 1400 °C for 6 h in air. Finally, they

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were naturally cooled to room temperature and ground for measurements.

2.2. Sample characterization

The phase purity of all samples was identified by using X-ray powder diffraction (XRD) analysis with a D2-PHASER diffractometer (Germany) operated at 10 mA and 30 kV with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The photoluminescence emission (PL) and excitation (PLE) spectra of the samples were obtained using a Fluorolog-3 Spectrofluorometer equipped with a 450 W Xe light source. The luminescence decay curves were measured by FLS-920T fluorescence spectrophotometer with a picosecond pulsed light emitting diode as the light source. In addition, in order to investigate the thermal stability of the BaZrSi $_3$ O $_9$:Bi $^{3+}$ phosphor, the thermal quenching was carried out using an aluminum plaque with cartridge heaters combination with PL equipment; the temperature was recorded by thermocouples inside the plaque and controlled with a standard TAP-02 high temperature fluorescence controller (Orient KOJI instrument Co., Ltd.).

3. Results and discussion

3.1. XRD analysis

The composition and phase purity of the as-prepared BaZrSi $_3$ O $_9$:xBi $^{3+}$ ($0.5\% \leq x \leq 10\%$) phosphors were identified by XRD. Fig. 1(a) shows the XRD patterns of BaZrSi $_3$ O $_9$:xBi $^{3+}$ ($0.5\% \leq x \leq 10\%$). It is found that all samples' powder diffraction patterns are in good agreement with the reference data (PDF#29-0214) except little excess peak at around 28° , indicating that BaZrSi $_3$ O $_9$:xBi $^{3+}$ remains a single phase when Bi $^{3+}$ doped in the BaZrSi $_3$ O $_9$ matrix under present investigation. A little excess peak may be due to formation of secondary phase consisting of part of unreacted ZrO $_2$ [21]. Besides, it is found that the positions of the diffraction peaks shift to high angle with increasing Bi $^{3+}$ doping concentrations, as shown in Fig. 1(b), which proves Bi $^{3+}$ ions enter Ba $^{2+}$ sites in BaZrSi $_3$ O $_9$. The ionic radius of Bi $^{3+}$ (103 pm) is smaller than that of Ba $^{2+}$ (135 pm) but larger than that of Zr $^{4+}$ (72 pm). When the Ba $^{2+}$ ions are occupied by Bi $^{3+}$ ions (1.03 \AA), causing the cell shrinkage, so the diffraction angle shift to higher angle.

3.2. Steady-state and time-resolved photoluminescence of BaZrSi $_3$ O $_9$:Bi $^{3+}$

Fig. 2 presents the PLE and PL spectra of BaZrSi $_3$ O $_9$:xBi $^{3+}$ ($0.5\% \leq x \leq 10\%$). The PLE spectra for all samples are almost same

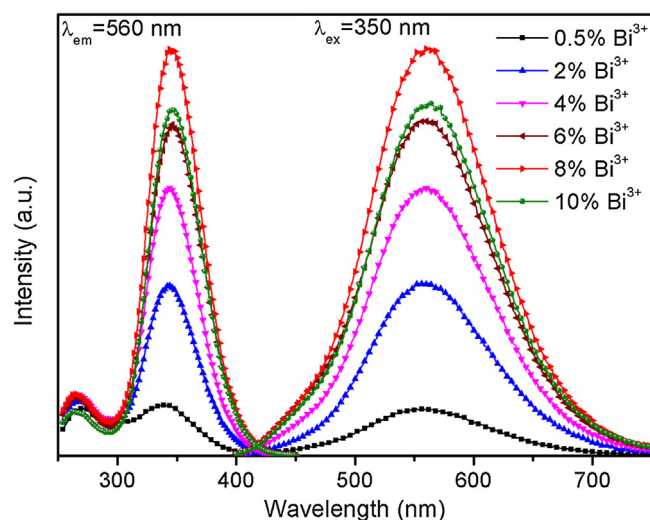


Fig. 2. PLE ($\lambda_{em} = 560 \text{ nm}$) and PL ($\lambda_{ex} = 350 \text{ nm}$) spectra of BaZrSi $_3$ O $_9$:xBi $^{3+}$ ($0.5\% \leq x \leq 10\%$).

except excitation intensity, all exhibit two strong absorption bands with maximum at 350 nm with a small shoulder at 267 nm. Based on the previous study of BaZrSi $_3$ O $_9$ based phosphor, it is considered that the small shoulder at 267 nm is attributed to Ti $^{4+}$ impurities [18–21], which exist in the starting material. The dominated broad excitation band at 350 nm is assigned to $^1S_0 \rightarrow ^3P_1$ transition of Bi $^{3+}$ [14,16]. Broad excitation wavelength make this phosphor may be suitable for application in White LEDs. Under 350 nm excitation, all samples show yellow emission with maximum around 560 nm (CIE chromaticity coordinates are around (0.40, 0.50)), which is due to $^3P_1 \rightarrow ^1S_0$ transition of Bi $^{3+}$. The PL intensity of Bi $^{3+}$ emission in BaZrSi $_3$ O $_9$:xBi $^{3+}$ ($0.5\% \leq x \leq 10\%$) is found to increase with the increase of Bi $^{3+}$ concentration, and starts to decrease when Bi $^{3+}$ concentrations exceeds 8% due to the concentration quenching effect [22,23]. In addition, the emission spectra also exhibits a small band about at 460 nm under 350 nm excitation. In order to further prove the existence of this small band, we have studied the emission spectra of BaZrSi $_3$ O $_9$:Bi $^{3+}$ with varying excitation wavelength as shown in Fig. 3. Along with the changes of excitation wavelength from 267 to 350 nm, the emission spectra vary from blue to yellow. As indicated in [18–21], the blue emission in fact originates from the Ti $^{4+}$ impurities, indicating that as-prepared BaZrSi $_3$ O $_9$:xBi $^{3+}$ sample have a weak blue emission from

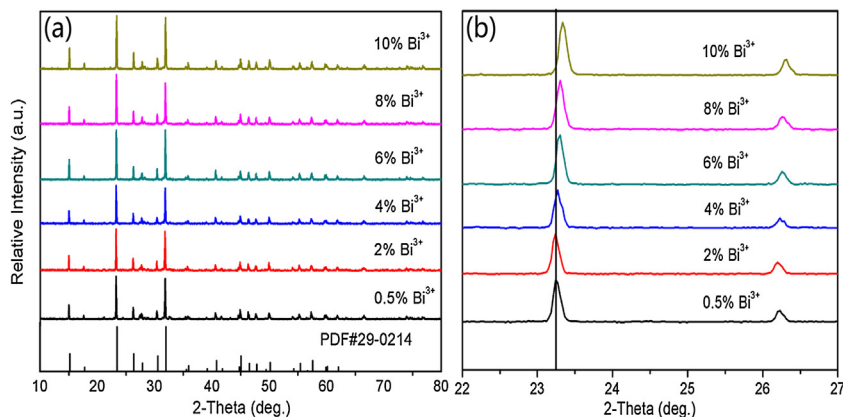


Fig. 1. XRD patterns of series BaZrSi $_3$ O $_9$:xBi $^{3+}$ samples.

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