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Eu^{3+}-doped highly thermal-stable barium yttrium aluminate as a red-emitting phosphor for UV based white LED

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HIGHLIGHTS

- $Ba_2YAlO_5:Eu^{3+}$ red-emitting phosphor was prepared.
- The excitation spectrum matches well with near-UV LED chips.
- The phosphor shows excellent thermal-stability.
- The red-emitting LED was fabricated based on the InGaN chip.

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ABSTRACT

A series of novel Eu^{3+} activated aluminate $Ba_2Y_{1-x}Eu_xAlO_5$ (x = 0.02–0.40) red-emitting phosphors were synthesized through a high-temperature solid-state route at 1380 °C. The phosphors were well crystallized in the space group $P2_1/c$ (No. 14). Their photoluminescence emission (PL) and excitation (PLE) spectra were investigated. The results indicate that the $Ba_2YAlO_5:Eu^{3+}$ phosphor can be excited effectively under 394 nm irradiation, which is suitable for UV LED chip. The obtained $Ba_2YAlO_5:Eu^{3+}$ phosphor shows four peaks, corresponding to the $^5D_0$–^7F_J (J = 0, 1, 2, 3 and 4) transitions of Eu^{3+} upon 394 nm excitation. The optimal doping concentration of Eu^{3+} in $Ba_2YAlO_5:xEu^{3+}$ was determined at 30 mol%. By temperature dependent emission spectra, the quenching temperature for $Ba_2YAlO_5:0.30Eu^{3+}$ was found to be over 500 K. And the CIE chromaticity coordinates of $Ba_2YAlO_5:0.30Eu^{3+}$ are very close to the National Television System Committee (NTSC) standard red.

1. Introduction

Recently, white light-emitting diodes (WLEDs) has gained enormous interest from scientists and engineers as a promising light source, which are important candidates for solid-state lighting due to its high luminous efficiency, compactness, long-lifetime, diversity design, fast switching good material stability and environmental friendly [1,2]. Currently, commercial w-LEDs is by combining an InGaN blue LED with $Y_3Al_5O_{12}:Ce^{3+}$ yellow-emitting phosphor [3]. But the above method infers some major disadvantages in the red spectral region, including low color rendering indexes (CRI, Ra < 80) and high correlated color temperature (CCT > 4500 K). To surmount these shortcomings, many oxynitride and nitride red phosphors seem to be potential candidates due to their highly chemically and thermally stable based on their rigid crystal structure. However, high cost arising from the harsh preparation condition and expensive reagents synthesis conditions of nitride compounds hinder their practical application [4–6]. Another effective method is to utilize near-UV LEDs chips coupled with multi-phosphors of red, green and blue [7–15].

Eu^{3+} ($4f^6$) ion as an important activator can provide an efficient and narrow band almost monochromatic light emission, which has been used in most commercial red phosphors. The desirable host material is essential for Eu^{3+} ion luminescence. Therefore, the crystal structure of the host aroused enormous strong interest. The aluminates have been extensively explored as hosts for phosphors due to their excellent optical properties. As the suitable host luminescent materials, aluminate have attracted much attention for the use of phosphors, such as $Ba_3Y_{1-y}Lu_yAl_2O_{7.5}:Ce^{3+}$ [16], $Sr_4Al_{14}O_{25}:Eu^{3+}$ [17], $Ba_3Al_2O_6:Eu^{3+}$ [18], $Gd_3Al_5O_{12}:Tb^{3+}$ [19], $MgSrAl_{10}O_{17}:Eu^{2+}$, Mn^{2+} [20], $Ca_2Mg_2Al_{28}O_{46}:Mn^{4+}$ [21], etc.

In this paper, we report the red emitting phosphors $Ba_2Y_{1-x}Eu_xAlO_5$ (x = 0.02–0.40) under NUV excitation. The phase purity and crystal

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structure, photoluminescence (PL) properties, influence of doping concentration, thermal stability, fluorescence decay, and chromaticity coordinate of the $Ba_2YAlO_5:Eu^{3+}$ phosphors were investigated.

2. Experimental procedure

The synthesis of powder samples $Ba_2Y_{1-x}Eu_xAlO_5$ (x = 0.02, 0.05, 0.10, 0.15, 0.20, 0.30, and 0.40) phosphors with the concentration of europium from 2 to 40 mol% was carried out via high-temperature solid-state reaction method. $BaCO_3$ (A.R.), Al_2O_3 (nanopowder, A.R.), Y_2O_3 (99.99%), and Eu_2O_3 (99.99%) were completely mixed and ground in an agate mortar. They were sintered in a furnace at 600 °C for 2 h in air atmosphere. The samples then were ground again and transferred into an alumina crucible heated at 1380 °C for another 5 h. When the samples were cooled to room temperature, they were ground slightly to obtain the phosphor powders. The associated reaction equations are as follows:

$$4BaCO_3 + (1-x)Y_2O_3 + Al_2O_3 + xEu_2O_3 \xrightarrow{1380^{\circ}C\times 5h} 2Ba_2Y_{1-x}Eu_xAlO_5$$

The phase purity of the as-prepared samples was identified via the XRD measurement on a Philips X'Pert MPD (Philips, Netherlands) with Cu Kα radiation (λ = 1.5418 Å) operated at 40 kV and Data collection was carried out in the range of 2θ = 10–70°. The morphology of the phosphors was measured using a scanning electron microscope (SEM, JEOL JSM-6490). Luminescence properties of the synthesized phosphors were performed at room temperature using a fluorescence spectrophotometer (HITACHI, F-4600) equipped with 150 W lamp at room temperature. The thermal quenching was also investigated by temperature-dependent photoluminescence intensity from 300 to 500 K. Luminescence decay curves of the samples were recorded by the Edinburgh FLS 920 spectrometer. The red LED was obtained in the method by combining near-UV InGaN chip with the prepared phosphor.

3. Results and discussion

The crystal structure of the Ba_2YAlO_5 was drawn by Diamond software and shown in Fig. 1, which have a pseudo-b. c. c. subcell as found for the perovskite structure ABX_3 [22]. They are monoclinic system and adopt space group $P2_1/c$ (14). Y^{3+} occupy 4e sites with six O atoms around them, forming [YO_6] octahedral and Al^{3+} in same Wyckoff 4e sites forms [AlO_4] tetrahedra. Y-O lengths are varied from 2.182 Å to 2.307 Å as shown in the Fig. 1(b). There are two Ba^{2+} sites in the structure with Ba^{2+} cations in 10-coordinate [23]. Overall, the structure of Ba_2YAlO_5 consists of alternating octahedral YO_6 layers and corner shared tetrahedral AlO_4 layers along the c axis and [YO_6] octahedron connects four [AlO_4] tetrahedral [24].

Fig. 2 shows the XRD pattern of $Ba_2YAlO_5:0.30Eu^{3+}$ along with the

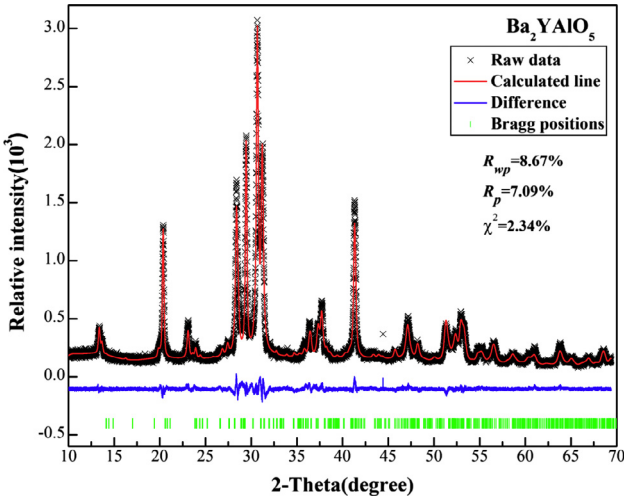

Fig. 2. Experimental XRD data, the corresponding Rietveld refine results, the Bragg reflections and the profile difference between experimental and calculated values of $Ba_2YAlO_5:0.30Eu^{3+}$ sample.

corresponding Rietveld structure refinement conducted by a general structure analysis system (GSAS) program. The refinement was proceeded by adopting the crystallographic data of Ba_2YAlO_5 (No.37-0292) as an initial model and converges to R_p = 8.67%, and R_{wp} = 7.09%, and χ^2 = 2.34, which indicates the refined atom position, fraction factors and temperature factors of the sample well satisfy the reflection conditions [22]. The final refined results confirm the single phase nature of the Ba_2YAlO_5 that is crystallized in a monoclinic $P2_1/c$ space group with lattice parameters of a = 13.1702 Å, b = 7.4539 Å, c = 5.7102 Å, and V = 527.22 Å^3, respectively. The effective ionic radius of Y^{3+} is 1.02 Å (CN = 6) and the ionic radius of Eu^{3+} is evaluated to be 1.06 Å (CN = 6) [25]. Given the similar charge and radius and identical valence, a possible substitution of Eu^{3+} ions to Y^{3+} ions might take place.

To examine the morphology of synthesized samples more precisely, scanning electron microscope of the samples were also carried out. Fig. 3 shows the representative SEM images of $Ba_2YAlO_5:Eu^{3+}$ phosphors. The sample crystallized with the smooth morphology and has some conglomeration aggregated for the high-temperature solid-state reaction. The particle sizes might be in micrometer ranges from a few to a few tens. After ball-milling of these phosphors, they will be easily bound to the substrate and lighting application.

Fig. 4 displays the diffuse reflectance spectrum of the as-prepared samples of Ba_2YAlO_5 compound and $Ba_2YAlO_5:0.30Eu^{3+}$ sample in the spectral region from 200 to 800 nm at room temperature. It can be

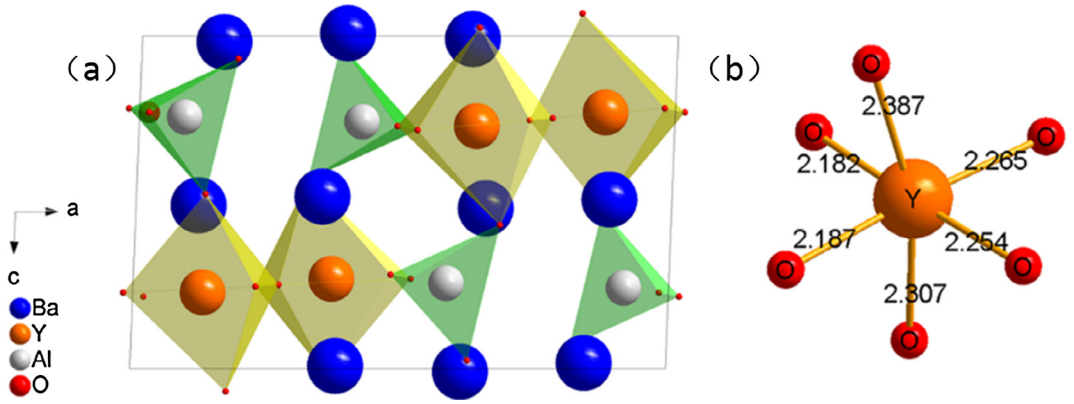

Fig. 1. (a) The schematic views of the Ba_2YAlO_5 structure along b-direction. (b) Coordination environment around Y. (The blue balls are barium atoms, the gray ones are aluminum atoms, the orange yttrium atoms, and the red ones are oxygen atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)