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Original research article

Synthesis and photoluminescence properties of a new orange-red emitting phosphor $KBa_2(PO_3)_5:Sm^{3+}$

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ABSTRACT

A series of Sm^{3+}-doped $KBa_2(PO_3)_5$ phosphors were synthesized successfully via high temperature solid-state reaction, and their structure, morphology and photoluminescence properties were investigated. The emission spectra consisted of several sharp emission peaks centered at 560 nm, 596 nm, 642 nm and 700 nm, which can be assigned to the characterize $f \rightarrow f$ transformations of Sm^{3+} activator. The strongest one at 596 nm corresponds to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition. The optimum dopant concentration of Sm^{3+} activator in $KBa_2(PO_3)_5$ host matrix is about 1 mol%. When the doping amount of Sm^{3+} was further increased, the concentration quenching phenomenon was observed. The CIE coordinates of $KBa_2(PO_3)_5$: $0.01Sm^{3+}$ phosphor was measured to be (0.5657, 0.4205), corresponding to orange-red color with a high color purity of about 90%. Hence, we may expect that the obtained phosphors $KBa_2(PO_3)_5:xSm^{3+}$ may be potentially used as an orange-red phosphor for white light-emitting diodes (w-LEDs).

1. Introduction

White light emitting diode (w-LED) is regarded as an efficient light emitting source in the 21 st century due to its conspicuous advantages, such as low cost, environmental friendly, excellent optical properties, energy saving, long lifetime, lower sintering temperature, high reliability, high thermal stability and so on, which have attracted more and more attentions [1–7]. It is well-known that the w-LEDs based on YAG:Ce^{3+} phosphors have been a commercial success for many years. However, it has a lowly satisfactory color-rendering index and poor optical properties because they are deficient in the red region [8–11]. In order to improve the performance of the w-LEDs, it is urgent to develop a good red phosphor that can be effectively pumped by the near-UV light device.

Sm^{3+}can get red or orange-red light under UV- or NUV-light when it was doped in different matrix materials. Beside the low cost, Sm^{3+} ion has a high absorption coefficient around 402 nm, and the main emission bands of $^4G_{5/2} \rightarrow {}^6H_j$ (j = 5/2, 7/2, 9/2, 11/2) fall in the visible range. In recent years, many Sm^{3+} doped materials such as $Ba_2Y_3(SiO_4)F_3:Sm^{3+}$ [12], $LaSr_2AlO_5:Sm^{3+}$ [13], $BaMoO_4:Sm^{3+}$ [14] etc., have been quickly developed to meet the needs w-LEDs as red or orange-red components. Moreover, the narrow emission band and high quantum efficiency ensure the application value of Sm^{3+} activated phosphor.

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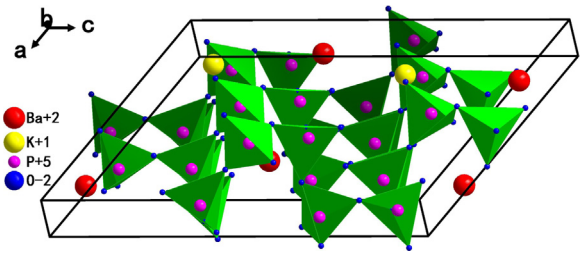

Fig. 1. The schematic views of $KBa_2(PO_3)_5$ crystal structure.

It has been reported that polyphosphate $KBa_2(PO_3)_5$ crystallizes in the acentric *Pc* space group with large second harmonic generation (SHG) coefficient [15]. The deep-ultraviolet transparent performance of $KBa_2(PO_3)_5$ is major advantage for using as a luminescent host matrix. However, to the best our knowledge, the $KBa_2(PO_3)_5:Sm^{3+}$ phosphor has never been reported so far. This work will report the synthesis, crystal structure, morphology and photoluminescence (PL) properties of phosphors $KBa_2(PO_3)_5:xSm^{3+}$ ($x = 0.003–0.06$).

2. Material and methods

2.1. Synthesis

Series of powder samples $KBa_2(PO_3)_5:xSm^{3+}$ ($x = 0.003$, 0.005, 0.01, 0.02, 0.05 and 0.06) were fabricated by a high temperature solid-state reaction at 750 °C. All of the reagents, KH_2PO_4 (Shanghai Reagent Factory, 99.99%), $BaCO_3$ (Shanghai Reagent Factory, 99.99%), $NH_4H_2PO_4$ (Shanghai Reagent Factory, 99.99%) and Sm_2O_3 (Sichuan Reagent Factory, 99.995%), were analytically pure from commercial sources and were used without further purification. The mixture of initial reagents was thoroughly ground in an agent mortar, and then was put into a platinum crucible in a muffle furnace. To begin with, the mixture was heated at the temperature of 400 °C for 10 h, and then heated treated at 750 °Cfor 80 h with several intermediate grindings to ensure a complete solid-state reaction.

2.2. Characterizations

All of the measurements were carried out at room temperature. The phase purities of as-prepared samples were analyzed by a D/MAX2500TC powder diffractometer using graphite-monochro-mated CuKα radiation in the angular range $2\theta = 5–70°$ with a step size of 0.05. The particle size and surface morphology were observed by scanning electron microscopy (SEM, KY-2800). The excitation and emission spectra were measured using a FLS920 Edinburgh Analytical Instrument apparatus. A standard Xe900 continuous-wave xenon lamp (450W) was used as the excitation source for steady-state measurements (stimulation slit width: 1.2 nm, emission slit width: 1.2 nm) with the step width of 1 nm and integration time of 0.2 s.

3. Results and discussion

3.1. Structural analysis

As shown in Fig. 1, $KBa_2(PO_3)_5$ crystallizes in a monoclinic space group of *Pc* and the crystal configuration is composed of one-dimensional (1D) infinite $[PO_3]_\infty$ chains, K^+ and Ba^{2+} ions [15]. The XRD patterns of phosphors with 0.003–0.06 Sm^{3+} concentrations and standard PDF#36-1478 of $KBa_2(PO_3)_5$ were presented in Fig. 2. It can be clearly observed that all peaks can be indexed to the pure $KBa_2(PO_3)_5$ phase and no impurity phase was observed in the samples when the doping concentration is below 0.06. Therefore, it can be concluded that the host crystal lattice are not changed by the Sm^{3+} dopant.

SEM is an important tool that utilizes focused beams of electrons to obtain the information of surface morphology and particle size [16]. Fig. 3 shows the surface morphology and particle size of $KBa_2(PO_3)_5:0.01Sm^{3+}$ phosphor at different magnifications. It can be observed that a microcrystalline structure with some agglomeration among crystalline grains is obtained by high temperature solid-state reaction. The average size of particles for $KBa_2(PO_3)_5:0.01Sm^{3+}$ phosphor was about 50 μm, which is available in the market contain particle size [17].

3.2. Excitation and emission spectra

Fig. 4 showed the excitation spectra of $KBa_2(PO_3)_5:0.01Sm^{3+}$ from 200 nm to 500 nm by monitoring emission of 596 nm. The excitation spectrum consists of a series of sharp peaks ranging from 275 nm to 500 nm, which correspond to the $4f \rightarrow 4f$ transitions of Sm^{3+} [18,19]: $^6H_{5/2} \rightarrow {}^4P_{5/2}$ (304 nm), $^6H_{5/2} \rightarrow {}^2L_{15/2}$ (316 nm), $^6H_{5/2} \rightarrow {}^4G_{7/2}$ (330 nm), $^6H_{5/2} \rightarrow {}^4H_{9/2}$ (343 nm), $^6H_{5/2} \rightarrow {}^4D_{3/2}$ (360 nm), $^6H_{5/2} \rightarrow {}^4D_{1/2}$ (373 nm), $^6H_{5/2} \rightarrow {}^4L_{15/2}$ (387 nm), $^6H_{5/2} \rightarrow {}^4F_{7/2}$ (400 nm), $^6H_{5/2} \rightarrow {}^4F_{5/2}$ (438 nm) and $^6H_{5/2} \rightarrow {}^4I_{11/2}$ (475 nm). Among these excitation transitions, $^6H_{5/2} \rightarrow {}^4F_{7/2}$ gives the strongest intensity, which matches well