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Synthesis and luminescence properties of $Y_{2.94}Al_{5-m}Ga_mO_{12}$:0.06$Ce^{3+}$ ($1 \le m \le 2.5$) green phosphors for white LEDs

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Abstract

A series of $Y_{2.94}Al_{5-m}Ga_mO_{12}$:0.06$Ce^{3+}$ ($1 \le m \le 2.5$) green phosphors were successfully synthesized by a solid-state reaction method. The microstructure, morphology, luminescence spectra and thermal stability of the phosphors were investigated. NaF flux can greatly promote the growth and crystallization of $Y_{2.94}Al_{5-m}Ga_mO_{12}$:0.06$Ce^{3+}$ ($1 \le m \le 2.5$) phosphors. The luminescence properties of $Y_{2.94}Al_{5-m}Ga_mO_{12}$:0.06$Ce^{3+}$ ($1 \le m \le 2.5$) green phosphors dramatically depend on the m value. When $m \le 1.5$, the phosphor shows strong luminescence and excellent thermal stability. At 150 °C, the luminescence intensity of the $m=1.0$ and $m=1.5$ samples still maintains 90.3% and 88.8% of that measured at 25 °C, respectively. The experimental results demonstrate that $Y_{2.94}Al_4GaO_{12}$:0.06Ce^{3+} and $Y_{2.94}Al_{3.5}Ga_{1.5}O_{12}$:0.06$Ce^{3+}$ are promising green phosphors, which have great potential for use not only in high color rendering index white LEDs but also in high-power white LEDs.

Keywords: Luminescence; Phosphors; YAGG:Ce; Thermal quenching; White LEDs

1. Introduction

White light-emitting diodes (LEDs) have been widely used to replace conventional incandescent and fluorescent lamps due to their excellent properties such as longer lifetime, higher efficiency, better reliability, and so on [1,2]. White LEDs are generally manufactured by combining blue LED chips and yellow-emitting cerium-doped yttrium aluminum garnet (YAG:Ce) phosphor. The main drawback of this type white LEDs is the low color rendering index (CRI), which is only about 75 [3,4].

There has been great interest in improving the CRI of white LEDs by replacing YAG:Ce phosphor with green phosphor and red phosphor simultaneously [5,6], which makes CRI value of the white LEDs exceed 90. So green phosphor is one of the key materials for making high CRI value white LEDs. It has been reported that $(Sr,Ba)_2SiO_4$:Eu^{2+} and $Lu_3Al_5O_{12}$:Ce^{3+} are good green phosphors for white LEDs [6,7]. However, $(Sr,Ba)_2SiO_4$:Eu^{2+} suffers from large thermal quenching of luminescence at high temperatures [8,9], which makes it unable to be used in high-power white LEDs. Although $Lu_3Al_5O_{12}$:Ce^{3+} shows excellent thermal stability, the main raw material of $Lu_3Al_5O_{12}$:Ce^{3+} phosphors is lutetium oxide (a rare earth oxide), which is very limited. Therefore, it is highly desirable to develop alternative green phosphors for white LEDs. It has been reported that Ce^{3+}-doped yttrium aluminum gallium garnet (YAGG:Ce) is able to emit green light when being excited by blue light [10], which suggests that YAGG:Ce phosphors may serve as a green phosphor for white LEDs.

It is well known that the luminescence intensity and the thermal stability (thermal quenching of luminescence and

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emission color stability) are very important parameters for evaluating the performance of a phosphor for white LEDs. However, to the best of our knowledge, there are few studies that systematically identify the Ga^{3+} concentration-dependent luminescence intensity and thermal stability of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ ($1 \leq m \leq 2.5$) phosphors for white LEDs. In this paper, we synthesized the phosphors by a solid-state reaction method. The effect of flux (BaF_2 and NaF) on microstructure of the phosphors was studied. The Ga^{3+} concentration-dependent luminescence intensity and thermal stability of the phosphors were systematically investigated. In addition, the luminescence intensity and thermal stability of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ ($1 \leq m \leq 2.5$) phosphors were compared with those of a commercially available $Y_3Al_5O_{12}:Ce^{3+}$ phosphor.

2. Experimental

2.1. Synthesis of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ phosphors

$Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ (m=1.0, 1.5, 2.0, and 2.5) phosphors were synthesized from the stoichiometric mixture of Y_2O_3 (99.99%), Ga_2O_3 (99.99%), Al_2O_3 (99.99%) and CeO_2 (99.99%), in which 4 wt% BaF_2 (99%) and 4 wt% NaF (99%) is used as flux, respectively. The mixture was mixed using a ball milling technique in aqueous media in a polymer bottle containing alumina ball. After mixing for 4 h, the slurry was transferred to a plastic container and dried at 100 °C for 16 h. The mixture powder was placed in alumina crucibles, and fired at 1500 °C for 4 h in a reducing atmosphere environment (75 v% H_2/25 v% N_2). After the cooling, the samples were crushed, and washed with hot distilled water (80 °C) for 3 times, and then dried at 100 °C for 12 h.

2.2. Characterization

The structure of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ (m=1.0, 1.5, 2.0, and 2.5) phosphors was analyzed by X-ray diffraction (XRD, Ultima IV, Rigaku) using Cu Kα_1 radiation. The morphology was observed by scanning electron microscopy (SEM, TM3000, Hitachi). The excitation and emission spectra were measured by a fluorescence spectrometer (FLS920, Edinburgh Instruments) with an Xe-lamp (450 W) as an excitation source. The luminescence intensity and the Commission Internationale de L'Eclairage (CIE) 1931 chromaticity coordinates at various temperatures (25–200 °C) were analyzed by an optical scanning spectrometer (Spectro320, Instrument Systems) with a narrow spectrum (FWHM=10 nm) blue LED (emission peak at 458 nm) as an excitation source. A self-designed heating attachment was employed to heat samples, which mainly includes a resistively heated sample holder and a standard temperature controller (error range of 0.1 °C).

3. Results and discussion

3.1. XRD of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ phosphors

The XRD patterns of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ (m=1.0, 1.5, 2.0, and 2.5) phosphors obtained with no flux, with 4 wt% NaF and with 4 wt% BaF_2 as flux are shown in Fig. 1. As shown in Fig. 1a and b, the diffraction peaks of the samples obtained with no flux and with 4 wt% NaF are matched well with those of the pure phase yttrium aluminum garnet ($Y_3Al_5O_{12}$ JCPDS 33-0040) and no detectable impurities or secondary phases are observed, which confirms that the obtained samples are single garnet phase. But as shown in Fig. 1c, there are some impurity phase peaks which are observed in all samples obtained with 4 wt% BaF_2 as flux. Although BaF_2 was proved to be excellent flux to synthesize YAG:Ce phosphor [11], our results indicate that BaF_2 is unsuitable for use as a flux to prepare $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ (m=1.0, 1.5, 2.0, and 2.5) phosphors. In addition, we note that the peak positions of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ (m=1.0, 1.5,

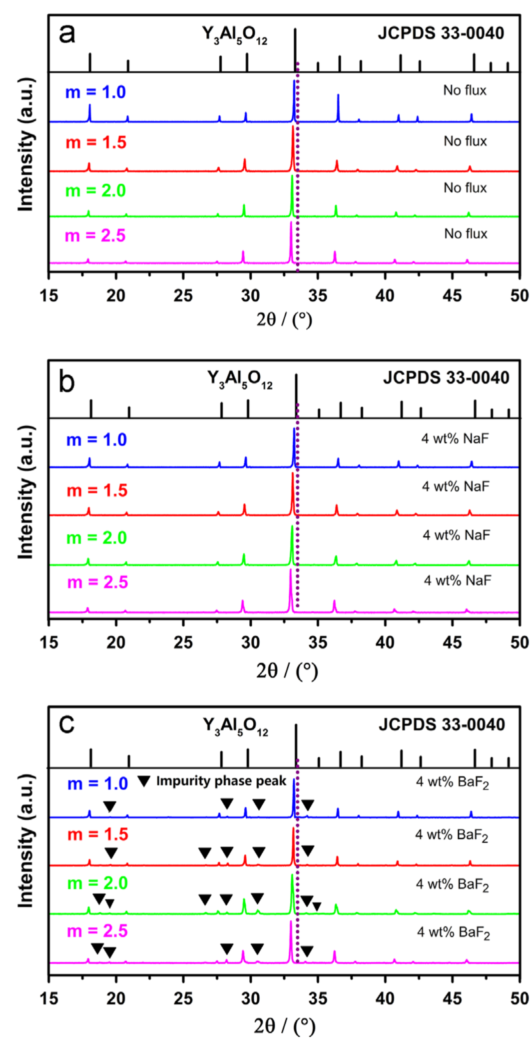

Fig. 1. XRD patterns of $Y_{2.94}Al_{5-m}Ga_mO_{12}:0.06Ce^{3+}$ (m=1.0, 1.5, 2.0, and 2.5) phosphors with no flux (a), with 4 wt% NaF (b) and with 4 wt% BaF_2 (c).