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Hydrothermal synthesis and luminescent properties of $BaTiF_6:Mn^{4+}$ red phosphor for LED backlighting

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ABSTRACT

The red-emitting phosphors $BaTiF_6:Mn^{4+}$ (denoted as BTFM) have been synthesized from HF, H_2TiF_6, Ba $(OH)_2$ and $KMnO_4$ mixed solution using a hydrothermal route. Their structure, composition and morphology were investigated. The photo-luminescent (PL) properties of the obtained BTFM products have been investigated, which exhibit broad excitation band in the blue region and sharp emission in the red region. In order to obtain the optimum BTFM red phosphor, many important factors of hydrothermal synthesis have been studied. The single red LED fabricated by combining BTFM with GaN chip shows intense red emission with the appropriate CIE chromaticity coordinates ($x = 0.660$, $y = 0.312$), and bright red light can be observed from the red LED. Therefore, this red phosphor may finds application in blue LED backlighting.

1. Introduction

Light emitting diodes (LEDs) have several advantages such as high efficiency, long service life, low energy consumption, and environment-friendly, which can be widely used in solid-state illumination, the backlight of liquid crystal display (LCD) and so on [1–4]. To obtain more natural illumination close to the sun light or incandescent lamps, the phosphor with a broad luminescence spectrum is favorable. However, for LED backlighting, such as the backlighting of LCD, luminescence with a narrow bandwidth is required to match with a transmittance spectrum of an optical filter [4]. Therefore, generally speaking, the adopted phosphors for LED backlighting should meet the following requirements: (1) intense broad excitation band corresponding to the emission of LED chip; (2) intense sharp emission with high color-purity.

Nowadays, the manufacturing technique for blue GaN chip is very mature, which is the most commercialized blue chips for fabricating white LEDs [5]. However, the study on the red phosphors excited by blue light is not sufficient. At present, there are two kinds of red phosphors that can be efficiently excited by blue light: the first is alkaline earth metal sulfides doped with Eu^{2+} phosphors [6–8], and the second is alkaline earth metal silicon nitride system [9–11]. The former one can be effectively excited by blue light (430–500 nm) to obtain a wide red emission (600–660 nm), but its unstable chemical properties, such as hydrolysis, oxidation, and sulfide precipitates, limits its applications in LEDs [6–8]. The latter one, for instance, $MAlSiN_3:Eu^{2+}$, $M_2Si_5N_8:Eu^{2+}$ and $MSi_2O_2N_2:Eu^{2+}$ (M = Ca, Sr, Ba) exhibiting high QE (quantum efficiency) and outstanding temperature properties, which satisfies the demands of white LEDs [9–11]. But its preparation needs extremely harsh conditions such as high temperature and reducing atmosphere. Furthermore, all the above mentioned red phosphors exhibit a broadband red emission, this limits their applications in LEDs backlighting. Therefore, it is urgent to explore new red phosphors with narrow bandwidth red emission under blue excitation.

As we known, Mn^{4+} ions are good luminescent centers in many phosphors [12–15]. These phosphors exhibit broad band in blue region which is due to its spin-allowed transition ($^4A2 \rightarrow {}^4T_2$), and red sharp emission which is ascribed to the electric-dipole-forbidden transition ($^2E_g \rightarrow {}^4A_2$) in octahedral site. The PL properties of Mn^{4+} well meet the requirement for LED backlighting.

In recent years, Mn^{4+}-activated alkaline/alkaline earth hexafluorometallate phosphors have been widely demonstrated since its excellent red emission under blue (~460 nm) light excitation [16–20]. For example, Pan's group investigated the synthesis method, optical properties and application for white LED of BTFM. As we know, though the doping amount of Mn^{4+} plays a crucial role

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on the PL properties of red phosphors doped with Mn^{4+}, it is complicated to be determined, especially when the obtained phosphors synthesized from hydrothermal route. Thus, in order to avoid direct measurement of doping amount in phosphor, we adopted an indirect method to systematically investigate the influence of some general and basic synthesis parameters, such as temperature, time, $KMnO_4$ and HF concentration on PL properties of as-synthesized phosphors. The optimum reaction condition for the preparation of this $BaTiF_6$:Mn^{4+} has been determined. Moreover, the application of this red phosphor on LED devices has been studied.

2. Experimental

2.1. Synthesis

The BTFM red phosphors were directly synthesized using a hydrothermal route. All the chemicals in this work, including 50% H_2TiF_6 aqueous solution, $KMnO_4$, $Ba(OH)_2$ and 40% HF aqueous solution were analytical grade without further purification prior to use. In a typical hydrothermal synthesis, 1.0 ml H_2TiF_6 aqueous solution, 0.065 g $KMnO_4$, 1.577 g $Ba(OH)_2{\cdot}8H_2O$, 50 ml HF aqueous solution were mixed thoroughly in a plastic cup for 15 min. Then the mixed solution was transferred into a Teflon cup, screwed in a stainless steel autoclave and kept at 180 °C for 8 h. After hydrothermal reaction, the autoclave was taken out of the oven and cooled naturally to room temperature. Finally, the postreaction solution was carefully filtered to collect the BTFM product, then washing this product using deionized water and methanol for several times and drying in 80 °C for 8 h.

The single red LED was fabricated by combining GaN chip with BTFM. Firstly, the mixtures of BTFM and epoxy resin (mass ratio is 1:1) was coated on GaN chip and solidified. Then the device was packaged with epoxy resin and solidified at 150 °C for 1 h. At last the red LED device was obtained.

2.2. Characterizations

The crystal structure was initially characterized using powder X-ray diffraction (XRD) with a X-ray diffractometer using Cu *Kα* radiation (λ = 0.15406 nm) and a graphite monochromator operating at 40 kV and 30 mA from 10° to 70° with a scanning step of 0.02° at 4° min^{-1}. The as-prepared products for morphologies and structures were observed by scanning electron microscopy (SEM, FEI Quanta 200 Thermal FE Environment scanning electron microscopy) with an attached energy-dispersive X-ray spectrometer (EDS). The XPS spectrum was recorded on an X-ray photoelectron spectroscopy (XPS, Phi5500, Ulvac-Phi, United States). Thermogravimetry (TG) and different scanning calorimeter (DSC) curves were measured on a Netzsch STA449C thermal analyzer at a heating rate 10 °C/min under N_2. Photoluminescence (PL) spectra were documented on a Cary Eclipse FL1011M003 (Varian) spectrofluorometer with the excitation and emission slits 2.5, and the xenon lamp was used as excitation source. The Diffuse Reflectance Ultraviolet-Visible spectrum (DRS) was collected on a Cary 5000 UV–Vis–NIR spectrophotometer, and the luminescence decay curve was obtained from an FLS920 fluorescence spectrophotometer. The performance of LEDs was recorded on a high accurate array spectrometer (HSP6000). All the measurements were performed at room temperature.

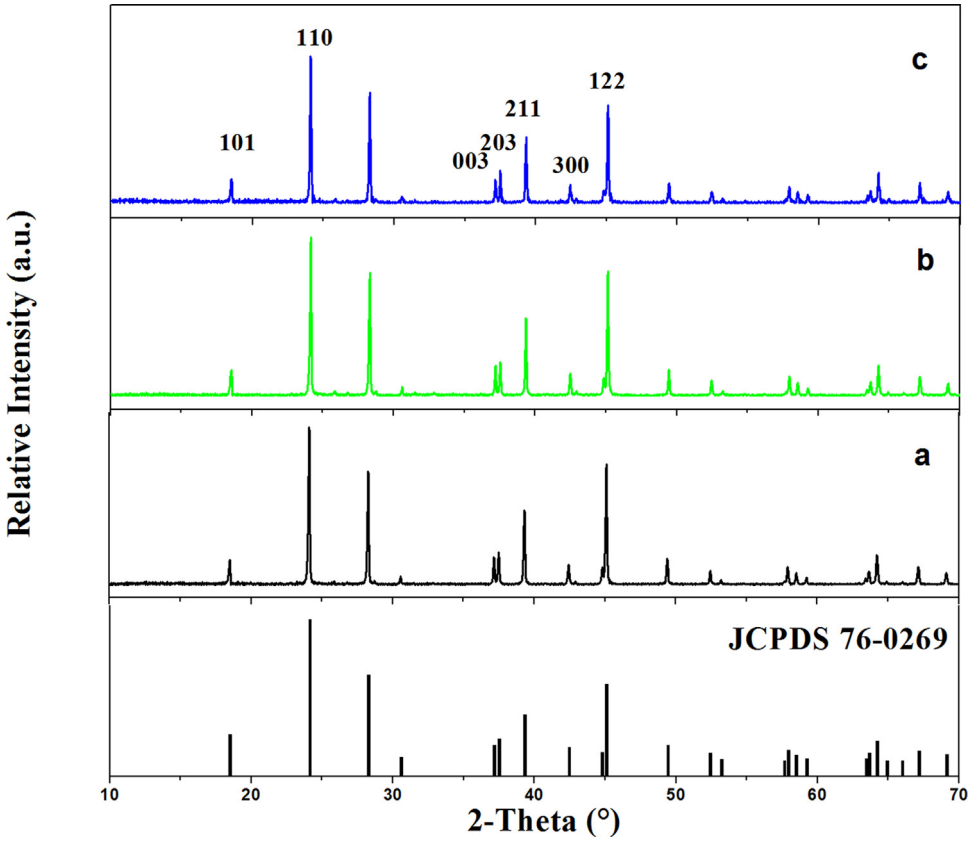

Fig. 1. XRD patterns of the red phosphors BTFM obtained from 40% HF without $KMnO_4$ (a), 8 mmol L^{-1} $KMnO_4$ in 10% HF (b) and 40% (c) by hydrothermal process at 180 °C for 8 h.