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White-light-emitting Eu^{2+} and Mn^{2+}-codoped silicate phosphors synthesized through combustion process

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Abstract

The $Ba_3MgSi_2O_8:Eu^{2+}$, Mn^{2+} phosphors are synthesized through combustion process with varying mixture ratio of citric acid and ethylene glycol used as a fuel to the used precursors. They have the mean particle size of 200 nm and the spherical shape. The $Ba_3MgSi_2O_8:Eu^{2+}$, Mn^{2+} phosphors show three emission colors: the blue color of 433 nm from Eu^{2+}(I) substituted by Ba^{2+}(I) site, the green color of 500 nm from Eu^{2+}(II, III) substituted by Ba^{2+}(II, III) site, the red color of 610 nm from Mn^{2+}(I, II, III). Compared with a solid-state method-prepared sample, the emission peaks of three emission bands are shifted to about 10 nm towards the shorter wavelength. This blue shift is explained by quantum size effect. The relative intensity ratios of the green band to the blue band are significantly increased as the increasing amount of fuel suggesting that Eu^{2+} ions in our sample preferably occupy Ba^{2+}(II, III) sites related to the green emissions.

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1. Introduction

White light-emitting diode (LED) has a number of advantages over the existing incandescent and halogen lamps in power efficiency, reliability and long lifetime [1]. White LED by the blue GaN-pumped yellow-emitting $(Y_{1-a}Gd_a)_3(Al_{1-b}Ga_b)_5O_{12}:Ce^{3+}$ phosphor has the following problems; changing color with input power, low color rendering index (CRI) due to two color mixing, and low reproducibility due to the strong dependence of color quality on quantity of phosphor. To solve these problems, the white LED has been fabricated by employing blue, green and red emitting multiphase phosphors excited by a ultraviolet (UV) InGaN chip [2,3]. This type of white LED has the following advantages; high color tolerance to UV chip's variation and excellent color rendering index due to white color generated by phosphors. For this application, silicate-based phosphors activated with Eu^{2+} or Mn^{2+} are very suitable [4]. These phosphors show broad emission colors through the transition of Eu^{2+} or Mn^{2+} activator strongly coupled to the host lattice. The absorption and emission bands of activators are also controlled by the host lattice crystal field [5]. The doped silicate-based phosphors with a maximum absorption of near ultraviolet give a wide range of white spectrum [4,5]. In addition, the morphology of phosphor for white LED greatly affects the luminescent efficiency because it influences the scattering of incident or emitting light. Phosphors with spherical shape are more effective for forming a good phosphor layer rather than irregular shaped one prepared by high temperature solid-state reaction [6]. A combustion synthesis technique is attractive technique because of this

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technique's success in producing fine particle size, crystalline, and homogeneous phosphor synthesized at relatively low temperature and with reduced processing time [7]. However, a few studies on the preparation of white-emitting silicate phosphors have been reported [8].

In this paper, we present the significant processing parameters of the combustion synthesis for producing white-emitting $Ba_3MgSi_2O_8:Eu^{2+}, Mn^{2+}$ phosphors with fine size and narrow size distribution. A blue shift behavior is observed in phosphors prepared by combustion process. The change in the relative intensity ratio of the green band to the blue band is increased as the increasing ratio of fuel to starting materials, and its origin is revealed in terms of the variation in the local structure.

2. Experimental details

Barium nitrate ($Ba(NO_3)\cdot 2H_2O$), magnesium nitrate($Mg(NO_3)_2\cdot 6H_2O$), europium nitrate ($Eu(NO_3)\cdot xH_2O$), and manganese nitrate ($Mn(NO_3)_2\cdot xH_2O$) were used as starting materials, respectively. Colloidal silica was used as the precursor of Si^{4+}. All precursors were dissolved in the solution of citric acid and ethylene glycol as fuel in combustion process. The molar ratios of $Eu^{2+}$and Mn^{2+} were kept as 0.01 and 0.05, respectively. The final solution was air dried for 24 h at 150 °C, and a combustion reaction was performed at 900 °C for 1 h under the air environment, and subsequently the reduction was performed at 900 °C for 1 h in a reducing atmosphere (a mixture of 25% H_2 and 75% N_2). Three different sets of samples were synthesized with various weight percent of the solution of citric acid and ethylene glycol used as a fuel to precursors of $Ba_3MgSi_2O_8:Eu^{2+}, Mn^{2+}$, i.e. (a) 85%, (b) 90%, (c) 95%. For comparison, $Ba_3MgSi_2O_8:Eu^{2+}, Mn^{2+}$ was also prepared at 1250 °C for 4 h in a reducing atmosphere through solid state reaction. The chemical composition was confirmed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Jobin Yvon 138 Ultrace). Phases of all samples were identified by MXP-3 XRD system (MAC Science. Co., Japan) with Cu_α radiation. The infrared spectrum was recorded on a Fourier-transformation infrared spectrophotometer (FT-IR)(Bruker, IFS 28CS) to determine amount of organic impurities. For the optical investigation, photoluminescence (PL) and photoluminescence excitation (PLE) measurements were obtained with a 200-W Xe-lamp as an excitation source. The morphology and the size of the obtained samples were observed with field emission-scanning electron microscopy (FE-SEM; Model S-47000, HITACH).

3. Results and discussion

FE-SEM images of the $Ba_3MgSi_2O_8:Eu^{2+}$ phosphor through combustion process with 90% of an optimal amount of the mixture of citric acid and ethylene glycol as a fuel (a), and the solid-reacted sample as a reference (b) are shown in Fig. 1. The combustion-driven particle has homogeneous and spherical shape, and its average particle size is about 200 nm, whereas the solid-reacted sample shows an irregular shape with a size of about 2 μm. Our phosphors with spherical shape can be effective for forming a good phosphor layer [6].

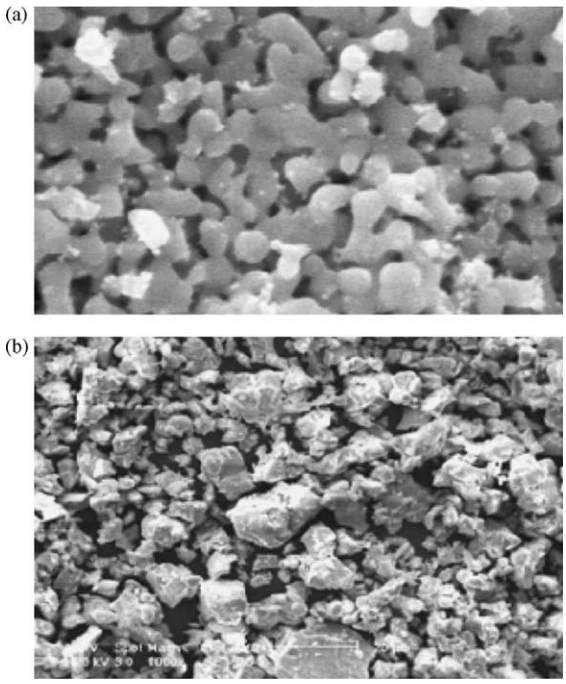

Fig. 1. FE-SEM images of combustion-driven (a) and solid-state reaction-driven $Ba_3MgSi_2O_8:Eu2^{2+}$ phosphors (b).

FT-IR spectra of the $Ba_3MgSi_2O_8:Eu^{2+}$ phosphors through combustion process with 90 and 95% of fuels are shown in Fig. 2. Broad peak around 3400 cm^{-1} corresponds

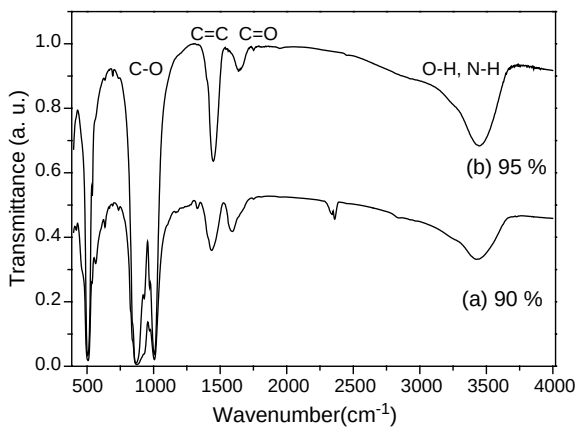

Fig. 2. FT-IR spectra of combustion-driven $Ba_3MgSi_2O_8:Eu^{2+}$ phosphors with the ratio of to starting materials with 90% (a) and 95% (b).