Materials Research Bulletin 107 (2018) 280–285

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Wide range yellow emission $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} phosphors for near ultraviolet white LEDs

Dorim Kim, Sungwook Park, Sung Heum Park, Byung Chun Choi, Jung Hwan Kim, Jung Hyun Jeong*

Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea

ARTICLE INFO

Keywords:
Luminescence
pc-LEDs
Quantum efficiency

ABSTRACT

A series of single phased phosphors $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} were synthesized by solid state reaction methods for applications of white light emitting diodes(w-LEDs). The broad absorption band at the near ultraviolet (NUV) region of 250–450 nm was obtained, which is ascribed to the $4f^7 \rightarrow 4f^65d^1$ electronic transition of the Eu^{2+} ions. Under NUV excitation, the broad yellow emission was obtained from tri-activated $Sr_8MgLa(PO_4)_7$ phosphors via combining three emission bands centered at 500, 550, and 600 nm contributed by Eu^{2+}, Tb^{3+} and Mn^{2+}, respectively. The optimized concentrations of Mn^{2+} and Tb^{3+} were 6 mol%, respectively, which enhanced the total PL intensity up to 30% comparing to only Eu^{2+} doped phosphor. Moreover, the quantum efficiency of $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} phosphor had achieved up to 52%. The combination of a NUV chip with compound of $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} and $BaMgAl_{10}O_{17}$:Eu^{2+} achieved tunable w-LEDs with high CRI. The results suggest that this single phased $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} phosphor can be a key for the phosphor converted w-LEDs for warm white light emission.

1. Introduction

In 1996, the Nichia Co. fabricated the blue LED with the yellow emission phosphor YAG:Ce^{3+} and developed white light emitting diodes (w-LEDs) [1]. Thereafter, the w-LEDs have attracted extensive interest as new generation lighting sources because of their environmental friendliness, energy saving, long operational lifetime, and high luminescence efficiency [2–5]. There are several methods of w-LEDs fabrications, the one is a yellow phosphor such as YAG:Ce^{3+} with blue LED chip, the others are one or more phosphor materials with NUV LED chip. The YAG:Ce^{3+} phosphor absorbs blue light radiated from the InGaN blue LED chip and converts them into yellow light. The combination of blue and yellow light produces white light. However, due to the lack of red light, the red emitting phosphors are the key materials to produce warm white light with low correlated color temperature values (CCT, 2700–4000 K) and high color rendering indices (CRI > 90) [6–8]. The other method to fabricate w-LEDs is the combination of near-ultraviolet chips (NUV, 360–420 nm) with various phosphors emitting yellow and blue colors (BAM:Eu^{2+}). Since the high efficiency from the efficient absorption in NUV wavelength, BAM:Eu^{2+} is widely used as the blue emitting phosphor. Therefore, it is important to find the new yellow emitting phosphors which absorbs the NUV region that has the ability to exhibit favorable properties including tunable CCTs and CIE chromaticity coordinates [9,10]. One of the strategies for generating yellow light is the Eu^{2+} activated phosphors. Eu^{2+} ion is characterized by intense broadband absorption in the NUV region and emits broadband from the blue to red emission wavelength assigned to the 4f-5d dipole allowed electronic transition of Eu^2 ions. Moreover, the color can be controlled by co-doping sensitizer of Mn^{2+} and Tb^{3+} in spite of the forbidden transition of Mn^{2+} and weak 4f-4f absorption transition at the region of 300–400 nm of Tb^{3+} [11–15].

In this paper, we propose an optimized $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} yellow emitting phosphor that well matches with BAM:Eu^{2+} blue phosphor for new warm white light. The crystal structure and optical properties of $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} were discussed by using X-ray diffraction (XRD), UV–vis spectrophotometer and photoluminescence(PL) spectra. The NUV LED chip fabricated with $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} phosphors has great potential to display warm white light. To the best of our knowledge, the $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} have not yet been reported in the literature.

* Corresponding author.
E-mail address: jhjeong@pknu.ac.kr (J.H. Jeong).

https://doi.org/10.1016/j.materresbull.2018.07.036
Received 27 April 2018; Received in revised form 20 July 2018; Accepted 28 July 2018
Available online 02 August 2018

2. Experiment

2.1. Synthesis

Single phased yellow phosphor $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} was prepared by the solid state reaction method. The precursors $SrCO_3$ (Sigma-Aldrich, 99.995%), $(MgCO_3)_4Mg(OH)_2{*}5H_2O$ (Sigma-Aldrich, 99.99%), La_2O_3 (Sigma-Aldrich, 99.99%), and $(NH_4)_2HPO_4$(Sigma-Aldrich, 99%), Eu_2O_3(Alpha aesar, 99.99%), $MnCO_3$ (Sigma-Aldrich, 99.99%) and Tb_4O_7(Sigma-Aldrich, 99.9%) were weighed as $Sr_{(8-x)}Mg_{(1-y-z)}La(PO_4)_7$: xEu^{2+}, yMn^{2+}, zTb^{3+} according to the stoichiometric quantity. The mixture of starting materials was extensively ground and placed into the alumina crucible. After preheating the mixture to 600 °C for 2 h to decompose the starting reagents and combustion of the constituents, the materials were heated at a rate of 5 °C min^{-1} and sintered at 1300 °C for 8 h under a reducing atmosphere of 5% H_2/95% Ar. The $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} phosphors were supplied by the Display and Lighting Phosphor Bank at Pukyong National University.

2.2. Characterization and optical measurements

The prepared phosphors were characterized by powder XRD with a Philips X'Pert multipurpose diffractometer (Philips, Netherlands) using CuK_α radiation (λ = 1.546 Å) for phase identification. The PL and PLE spectra were recorded by a Photon Technology International Fluorimeter (PTI, USA) with a 60 W Xe-arc lamp as the excitation light source. Diffuse reflectance spectra (DRS) were obtained from UV–vis spectrophotometer (JASCO, V-670). The electroluminescence (EL) spectra were obtained using a luminance meter (TOPCON SR-3AR, JAPAN) at a constant DC current. All of the measurements were performed at room temperature.

2.3. W-LED fabrication

The w-LEDs were fabricated by integrating a mixture of transparent silicone resin with yellow emitting phosphor $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} and blue emitting phosphor $BaMgAl_{10}O_{17}$:Eu^{2+} on NUV chip (Product No:9LEUVV516TA6).

3. Results and discussion

3.1. Phase characterization

The XRD patterns of incorporation of Eu^{2+}, Mn^{2+} and Tb^{3+} ions in the host are illustrated in Fig. 1(a). In spite of the incorporation, it did not derive any significant changes in the host structure. This result indicates that the crystal structure retains to be the single phase despite of doping Eu^{2+}/Mn^{2+}/Tb^{3+} in the host. The structure parameters of $Sr_8MgLa(PO_4)_7$ and $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} were refined by the Rietveld method from X-ray diffraction data. The initial structural model was constructed with standard data in the Inorganic Crystal Structure Database (ICSD) file no. 59722 [11–13]. The calculated (solid line), observed (crosses), and difference (bottom) XRD profiled for the Rietveld refinement of $Sr_8MgLa(PO_4)_7$ and $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} phosphors are illustrated in Fig. 1(b) and (c), respectively. According to the result of Rietveld refinement, the crystal structure of $Sr_8MgLa(PO_4)_7$ has a monoclinic structure on the basis of space group I2/a with parameter a = 18.8684 Å, b = 10.5549 Å, c = 18.2802 Å. β = 133.0153°. The observed XRD peaks of fit parameters are R_{wp} = 6.54% and R_p = 4.65%. The crystal structure of $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} has a monoclinic structure on the basis of space group I2/a with parameter a = 17.9439 Å, b = 10.5999 Å, c = 18.3668 Å. β = 132.9395°. The observed XRD peaks of fit parameters are R_{wp} = 4.46% and R_p = 3.23%. The refinement parameters of $Sr_8MgLa(PO_4)_7$ and $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} are listed in Table 1. The simulation of the crystal structure by using Rietveld refinement is shown in Fig. 1(d). According to the result, the structure of $Sr_8MgLa(PO_4)_7$ are isostructure with β-$Ca_3(PO_4)_2$. The β-$Ca_3(PO_4)_2$ structure has five different types of independent cation sites, the Sr(1) is defined as 5-fold coordination, Sr(2)/Sr(3) are defined as 6-fold coordination, and Sr(4)/Sr(5) is defined as 7-fold coordination. The ionic radius for the 6-coordinated Sr(2)/Sr(3) sites are 1.18 Å and for the 7-coordinated Sr(4)/Sr(5) sites are 1.21 Å. Similarly, the ionic radius of Eu^{2+} has 1.17 Å with CN = 6, 1.20 Å with CN = 7 [12]. Due to the similarities of the ionic radius between Eu^{2+} with Sr^{2+}, the Eu^{2+} ions are expected to occupy Sr^{2+} ion sites in the $Sr_8MgLa(PO_4)_7$. Moreover, both of the Mn^{2+} and Tb^{3+} ions can be easily substituted in site of Mg^{2+} due to the similar ionic radii of Mn^{2+} (0.66 Å) and Tb^{3+} (0.92 Å) with Mg^{2+} (0.72 Å).

3.2. PL properties

The optimized composition of Eu^{2+} dopant in $Sr_8MgLa(PO_4)_7$ was determined to be 3 mol% [16]. The PL intensity centered at 600 nm had increased with the increase of Mn^{2+} ($^4T_1 \rightarrow {}^6A_1$ transition) content up to a maximum value of 6 mol% as shown in Fig. 2(a). The PL intensity centered at 550 nm had increased with the increase of Tb^{3+} ($^5D_4 \rightarrow {}^7F_J$ transition) content up to a maximum value of 6 mol% as shown in Fig. 2(b). The quantum efficiency (QE) by co-doping Mn^{2+} and Tb^{3+} to $Sr_8MgLa(PO_4)_7$: Eu^{2+} are illustrated in Fig. 2(c). The QE was found to be up to 35%, 38% and 52% by doping Eu^{2+}, Eu^{2+}/Mn^{2+} and Eu^{2+}/Mn^{2+}/Tb3$^+$, respectively. Moreover, by co-doping Mn^{2+} and Tb^{3+} to $Sr_8MgLa(PO_4)_7$: Eu^{2+} not only enhanced total luminescence intensity to 30% (illustrated in inset of Fig. 2(c)) but also consist low CCT up to 3500 K.

Fig. 3(a) illustrates the photoluminescence (PL) spectra of $Sr_8MgLa(PO_4)_7$: Eu^{2+}, Mn^{2+}, Tb^{3+} and the Gaussian components under 365 nm excitation. According to the environment of $Sr_8MgLa(PO_4)_7$ structure, the PL spectra of the phosphor can be deconvoluted into five Gaussian profiles with peaks centered at 480, 500, 525, 590 and 680 nm [17,18]. The broad emission spectrum of $Sr_8MgLa(PO_4)_7$ in the wavelength range of 450–750 nm is attributed to the $4f^65d^1 \rightarrow 4f^7$ electronic transition of the Eu^{2+} ions. The energy widely varies with the lattice in the Eu^{2+} ions doped phosphors due to the combined effect of the centroid shift and the crystal field splitting of the 5d states [19]. The crystal field splitting is related to coordination number, radius of the host cation, polyhedron shape and size. There are two kinds of theoretical approach to the crystal field splitting [20–23]. Here, the simple method of was employed in this study. The possible crystallographic sites published by Van Uitert [24–27] can be theoretically investigated by the following equation:

$$E(cm^{-1}) = Q^*\left[1-\left(\frac{V}{4}\right)^{1/V} \times 10^{-(nE_a r)/80}\right]$$

Where, E represents the position of the d band edge in energy for the rare earth ion (cm^{-1}), Q^* is the energy position for the lower d band edge for the free ion (Q^* = 34,000 cm^{-1} for Eu^{2+}), V is the valence of the activator (Eu^{2+}) ion (V = 2 for Eu^{2+}), n is the number of anions in the immediate shell around Eu^{2+} ion, E_a is the electron affinity of the atoms that form anions (2.2 eV) and r is the radius of the host cation (Sr^{2+}) replaced by the Eu^{2+} ion (in pm). The equation demonstrates the tendency that E increases as the ligand field of the Eu^{2+} ion decreases with the increase in (n × r). Here, r values of Sr(2)/Sr(3) and Sr(4)/Sr(5) were calculated to be 118 pm and 121 pm, respectively. The emissions around 502 nm were attributed to a 7-coordinated Eu^{2+} ion occupying the Sr(4)/Sr(5) site, the emission band around 536 nm were attributed to a 6-coordinated Eu^{2+} ion occupying the Sr(2)/Sr(3) site and the longest emission band centered at 680 nm can be predicted to be due to the 5-coordinated Eu^{2+} ion occupying the Sr(1) site. The experimental and calculated emission wavelengths of Eu^{2+} in two