Dyes and Pigments 160 (2019) 234–242

Contents lists available at ScienceDirect

Dyes and Pigments

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

Structural and photoluminescence properties of $La_{1-x}NaCaGa_3PZrO_{12}$ doped with Ce^{3+}, Eu^{3+}, and Tb^{3+}

D.A. Hakeem[a], J.W. Pi[a], G.W. Jung[a], S.W. Kim[b,*], K. Park[a,**]

[a] Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, 142-747, Republic of Korea
[b] Electronic Convergence Materials Division, Optic & Display Materials Center, Korea Institute of Ceramic Engineering and Technology, Jinju-si, Gyeongsangnam-do, 52851, Republic of Korea

ARTICLE INFO

Keywords:
$LaNaCaGa_3PZrO_{12}$
Phosphor
Emission
Photoluminescence

ABSTRACT

In this work, $LaNaCaGa_3PZrO_{12}$ was explored as a host material of phosphors for white-light-emitting diode (WLED) applications for the first time. Rare-earth metal ions (Ce^{3+}, Eu^{3+}, and Tb^{3+}) doped garnet $LaNaCaGa_3PZrO_{12}$ phosphors were fabricated by a solid-state reaction method. The structural and photoluminescence properties of the prepared garnet phosphors were investigated. The Ce^{3+}-, Eu^{3+}-, and Tb^{3+}-doped $LaNaCaGa_3PZrO_{12}$ phoshors emitted blue, red, and green light, respectively, and are promising for WLED device applications.

1. Introduction

White-light-emitting diodes (WLEDs) are considered the next generation light source due to their high brightness, low electricity consumption, high energy efficiency, long operational lifetime, light stability, and environmentally friendly characteristics [1–5]. The first approach to fabricate WLED devices is to combine a blue InGaN chip with a yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) garnet phosphor [6–9]. The YAG:Ce phosphor shows excellent chemical stability, high quantum efficiency, short lifetime, high creep resistance, and high optical isotropy [10,11]. An alternative approach is to combine a blue or near-ultraviolet (UV) LED chip with multichromatic blue, green, and red phosphors to generate white light. At present, $Y_2O_2S:Eu^{3+}$ (red), $SrAl_2O_4:Eu^{2+}$ (green), and $BaMgAl_{10}O_{17}:Eu^{2+}$ (blue) phosphors are employed in WLEDs. However, this approach faces several problems, including a poor color rendering index (< 80) as a result of the lack of red light, low blue/yellow color separation, and low luminous efficiency [12]. Therefore, over the past several decades, vanadates, phosphates, silicates, borates, aluminosilicates, nitrides, molybdates, tungstates, and zirconates have been investigated for use as hosts in WLEDs [13–19]. The performance of WLEDs depends strongly on the quality of the white light produced by phosphors. As a result, the fabrication of high-quality phosphors for WLEDs applications is a hot issue.

The purpose of this study is to develop new garnet phosphors for WLED applications. To achieve this purpose, we designed and explored a new garnet host material of phosphors for WLED applications. The equations given by Hawthorne [20] were used to screen and design new garnet phosphors. He reported that for the formation of garnet phosphors, a positional parameter (x, y) should be located inside or on the ellipse in the x- and y-coordinates. In this study, we explored $LaNaCaGa_3PZrO_{12}$ as a host material for the first time, based on Hawthorne's criteria. Rare-earth metal ions (Ce^{3+}, Eu^{3+}, and Tb^{3+}) doped garnet $LaNaCaGa_3PZrO_{12}$ phosphors were fabricated by a solid-state reaction method. Rare-earth metals have fully filled outer (5s and 5p) electronic shells shielding an unfilled inner (4f) orbital, thereby allowing rare-earth metal ions doped materials to show characteristic optical properties [21]. We studied the structural and photoluminescence (PL) properties of Ce^{3+}-, Eu^{3+}-, and Tb^{3+}-doped $LaNaCaGa_3PZrO_{12}$ garnet phosphors. As far as we know, there exists no report on studying the structural and PL properties of Ce^{3+}-, Eu^{3+}-, and Tb^{3+}-doped $LaNaCaGa_3PZrO_{12}$ garnet phosphors.

2. Experimental

$La_{1-x}NaCaGa_3PZrO_{12}:xLn^{3+}$ (Ln = Ce, Eu, and Tb) phosphors were prepared through the solid-state reaction process. The starting materials used in this process were as follows: La_2O_3 (High Purity Chemical, 99.99%), Na_2CO_3 (High Purity Chemical, 99%), $CaCO_3$ (High Purity Chemical, 99%), Ga_2O_3 (High Purity Chemical, 99.9%), $(NH_4)_2HPO_4$ (Samchun Chemical, 99%), $ZrO(NO_3)_2$ (High Purity Chemical, 98%),

* Corresponding author.
** Corresponding author.
E-mail addresses: skim80@kicet.re.kr (S.W. Kim), kspark@sejong.ac.kr (K. Park).

https://doi.org/10.1016/j.dyepig.2018.06.047
Received 4 April 2018; Received in revised form 21 June 2018; Accepted 28 June 2018

K_2CO_3 (High Purity Chemical, 99%), CeO_2 (High Purity Chemical, 99.99%), Eu_2O_3 (High Purity Chemical, 99.9%), and Tb_4O_7 (High Purity Chemical, 99%). An appropriate amount of the starting materials was weighed and homogenously mixed for 30 min by using a pestle and mortar. The mixed powders were transferred to alumina crucibles and then calcined at 600 °C for 5 h. A small quantity of K_2CO_3 flux (10 wt %) was added to the calcined powder. The resultant powders were annealed at 1350 °C for 12 h.

The crystal structure of the prepared garnet phosphors was analyzed using an X-ray diffractometer (XRD; Rigaku RINT2000, Japan) with Cu K_α radiation (λ = 1.5406 Å). For Rietveld refinement, XRD patterns were obtained with an X-ray diffractometer (XPERT-PRO, Pananalytical, UK) with Cu K_α radiation (λ = 1.5406 Å) and operating at 40 kV and 30 mA over a wide 2θ range from 5°–145° with a scan speed of 0.01313°/m. The experimental XRD data were refined using the Rietveld method with a least-squares fitting approach [22]. The refinement of the $LaNaCaGa_3PZrO_{12}$ (taken as an example) was carried out by using the FULLPROF software as the running program [23]. The PL spectra of the phosphors were obtained with a spectrofluorometer (FS-2, Scinco Co., Korea) equipped with a xenon lamp. The internal quantum efficiency (IQE) of the prepared samples was measured with a spectrofluorometer (DARSA PRO-5200 System, PSI Co., Ltd, Korea). To investigate the thermal quenching from 30 °C to 150 °C, the same spectrofluorometer (DARSA PRO-5200 System) with a heating cell was used. All emission spectra were obtained using the same amount of the prepared phosphors and recorded under the same conditions. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinate (*x, y*) was calculated from the observed emission spectra by using a CIE calculator. In addition, the values of correlated color temperature (CCT) and color purity were calculated with the CIE coordinate (*x, y*) data obtained.

3. Results and discussion

3.1. Selection of $LaNaCaGa_3PZrO_{12}$ as a host material

Inorganic garnet materials with a general formula $\{L\}_3[M]_2(N)_3O_{12}$ possess a cubic crystal structure, belonging to the $Ia\bar{3}d$ space group. The notations {L}, [M], and (N) represent the cations that occupy three different crystallographic sites, i.e., {L} for the eight-coordinated dodecahedral site (24c), [M] for the six-coordinated octahedral site (16a), and (N) for the four-coordinated tetrahedral site (24d). To figure out the novel garnet phosphors, Hawthorne [20] derived the positional parameters of the cations in oxide garnet phosphors in 1981, based on the mean ionic radii of the cations that occupy at the {L}, [M], and (N) sites of garnet phosphors using multiple regression analysis, as follows:

$$x = 0.0278(22)\ r\{L\} + 0.0123(28)\ r[M] - 0.0482(16)\ r(N) + 0.0141. \quad (1)$$

$$y = -0.0237(25)\ r\{L\} + 0.0200(32)\ r[M] + 0.0321(18)\ r(N) + 0.0523 \quad (2)$$

$$z = -0.0102(20)\ r\{L\} + 0.0305(25)\ r[M] - 0.0217(14)\ r(N) + 0.6519 \quad (3)$$

where r{L}, r[M], and r(N) are the ionic radii of the cations at the dodecahedral, octahedral, and tetrahedral sites, respectively. The positional parameter (*x*, *y*) of $LaNaCaGa_3PZrO_{12}$ was calculated to be (0.0354, 0.0496), which is located inside the ellipse in the *x*- and *y*-coordinates. This finding means that the positional parameter (*x*, *y*) satisfies a criterion for the selection of suitable garnet phosphors. Therefore, in this study, we selected $LaNaCaGa_3PZrO_{12}$ as a host material and then studied the structural and PL properties of Ce^{3+}-, Eu^{3+}-, and Tb^{3+}-doped $LaNaCaGa_3PZrO_{12}$ phosphors.

The structural parameters were determined with the Rietveld refinement method using FULLPROF software [23]. The experimental and calculated profiles of the $LaNaCaGa_3PZrO_{12}$ selected as a host material are shown in Fig. 1. To refine the XRD pattern of $LaNaCaGa_3PZrO_{12}$, the crystallographic data of $Ca_2LaZr_2Ga_3O_{12}$ with a garnet structure were used as the initial structure model [24]. In Fig. 1, the "■" marks indicate the observed diffraction data; the red solid curves represent the calculated diffraction data; the green vertical lines indicate the positions of the simulated diffraction patterns; and the blue solid line denotes the deviation between the observed and calculated values. Rietveld analysis confirmed that the $LaNaCaGa_3PZrO_{12}$ crystallizes in a cubic crystal structure and $Ia\bar{3}d$ space group. The lattice parameters of the $LaNaCaGa_3PZrO_{12}$ (a = b = c = 12.78 Å) were quite similar to those of the $Ca_2LaZr_2Ga_3O_{12}$ garnet (a = b = c = 12.75 Å) [24]. A schematic crystal structure of $LaNaCaGa_3PZrO_{12}$ after refinement is shown in Fig. 1(b). The refined structural parameters, including the atomic position, thermal parameter (B_{iso}), and occupancy of the constituent atoms, of $LaNaCaGa_3PZrO_{12}$ are given in Table 1. The La, Na, and Ca cations occupy the dodecahedron site; the P and Zr cations occupy the octahedron site; and the Ga cations occupy the tetrahedron site.

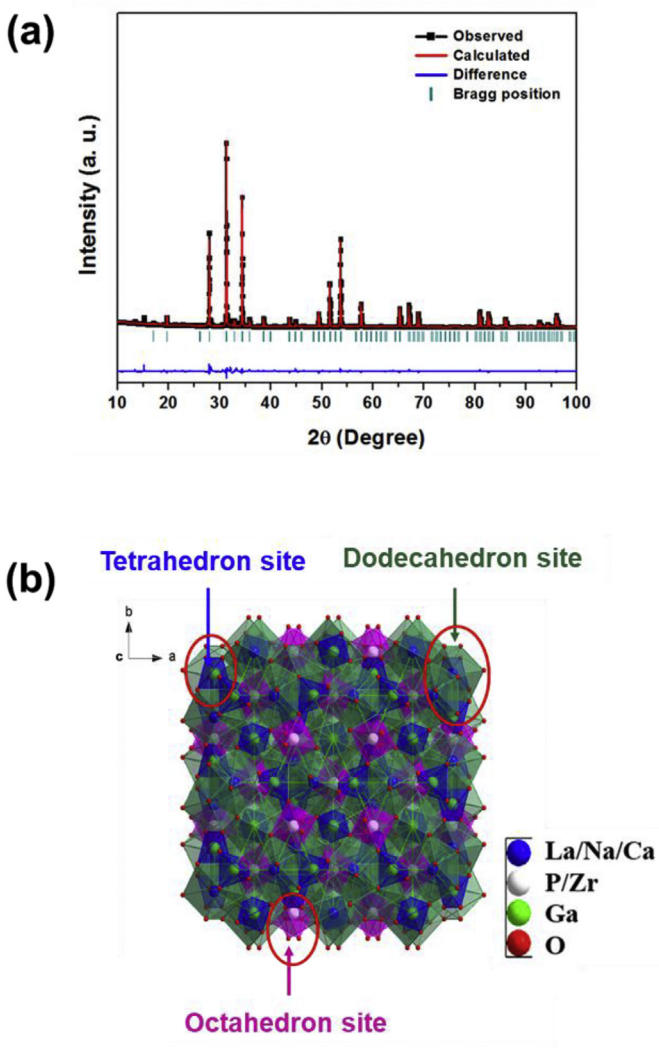

Fig. 1. (a) Rietveld refinement of $LaNaCaGa_3PZrO_{12}$ showing the observed data (■), calculated data (red solid line), and difference (blue solid line) profile and (b) the crystal structure representation of $LaNaCaGa_3PZrO_{12}$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)