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UV excitation band induced novel $Na_3Gd(VO_4)_2:RE^{3+}$ ($RE^{3+} = Eu^{3+}$ or Dy^{3+} or Sm^{3+}) double vanadate phosphors for solid-state lightning applications

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ABSTRACT

The $Na_3Gd(VO_4)_2$ (NGVO):RE^{3+} ($RE^{3+} = Eu^{3+}$ or Dy^{3+} or Sm^{3+}) single doped phosphor materials were synthesized by a citrate-based sol-gel method. The phase formation of NGVO host lattice at different calcination temperatures was analyzed by X-ray diffraction results, which confirmed a monoclinic phase with a space group of $P21/c$ (14). The field-emission scanning electron microscope image of the NGVO sample revealed an agglomerated morphology which was further analyzed by its corresponding energy dispersive X-ray spectrum. Under ultraviolet excitations, the photoluminescence (PL) properties of NGVO:Eu^{3+}, NGVO:Dy^{3+} and NGVO:Sm^{3+} phosphors exhibited intense red, yellow and reddish-orange emissions at 618, 575 and 646 nm owing to their characteristic $^5D_0 \rightarrow {}^7F_2$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ electronic transitions, respectively. The optimum doping concentrations of Eu^{3+}, Dy^{3+} and Sm^{3+} ions in the NGVO host lattice were determined to be 0.09, 0.02 and 0.01 mol, respectively. Dexter's theory demonstrates that the quadrupole interactions are responsible for the concentration quenching mechanism in the NGVO:Dy^{3+} and NGVO:Sm^{3+} phosphors. Furthermore, Commission International de l'Eclairage chromaticity diagram was obtained and temperature-dependent PL emission spectra were measured for the optimal NGVO:Eu^{3+}, NGVO:Dy^{3+} and NGVO:Sm^{3+} phosphors.

1. Introduction

Solid-state lightning based on white light-emitting diodes (WLEDs) has been greatly renowned as a next-generation light source to replace the conventional incandescent and fluorescent lamps owing to their low power consumption, high brightness, long working lifetime and eco-friendly feature [1–5]. Many research works have been devoted because the WLEDs obtained with these excellent features can save the energy above 80% and have the longer working lifetime when compared with the traditional fluorescent lamps [6,7]. In general, there are two ways to fabricate the WLEDs. One is the combination of a InGaN blue LED chip with the Ce^{3+} ions induced yttrium aluminum garnet ($Y_3Al_5O_{12}:Ce^{3+}$) yellow-emitting phosphors and this approach offers cool white light with high efficiency, high correlated color temperature and poor color-rendering index (CRI) value (<80) which is caused due to the inadequacy of the green and red luminescence in the longer wavelength regions [8–10]. In order to overcome the poor CRI property, the second approach has been established. In this type of study, the WLEDs have been developed by the combination of an ultraviolet (UV)-based LED chip with the trichromatic (red/green/blue) phosphors, exhibiting high CRI value with excellent power output for back light source applications [11,12]. Hence, the high luminescence efficiency of trichromatic (red/green/blue) phosphors prepared under UV excitations provides the high-performance WLEDs. Nevertheless, high-quality trichromatic phosphors under UV excitation wavelengths are still inadequate and persist as a challenging task.

Trivalent rare-earth (RE^{3+}) ions activated inorganic functional groups are promising host lattice materials to prepare the trichromatic phosphors because of their distinct $4f^n$ electronic configurations and good luminescence properties [13,14]. Among the different RE^{3+} ions, Eu^{3+}, Dy^{3+} and Sm^{3+} are good active species to produce red, yellow and orange colors, respectively, to emphasize the trichromatic phosphor-based WLEDs. Recently, self-activated vanadates have been widely investigated as a new kind of

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phosphors from the commercial red-emitting $YVO_4:Eu^{3+}$ phosphors. Additionally, vanadate phosphors show broadband luminescence from 400 to 700 nm under UV or near-UV excitations. A class of RE^{3+} ions doped double vanadate group phosphors such as $K_3Y(VO_4)_2:Eu^{3+}$ [15], $K_3RE^{3+}(VO_4)_2(RE^{3+} = Sc^{3+}, Y^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+}, Lu^{3+}$ or $Tm^{3+})$ [16] $CsK_2Gd(VO_4)_2:Eu^{3+}$ [17] and $KLa_5O_5(VO_4)_2:Eu^{3+}$ [18] have been proved as a good host lattice material to exhibit excellent optical properties. The central metal V^{5+} ions in the VO_4^{3-} group surrounded by 4 oxygen anions to make a tetrahedral symmetry (T_d) and the VO_4^{3-} clusters show visible emission under UV excitation wavelengths. In the same manner, a novel inorganic double vanadate group host lattice material having chemical composition of $Na_3Gd(VO_4)_2$ with a monoclinic structure could be expected as a promising luminescent material for UV-based WLEDs.

As we know, RE^{3+} ions doped phosphor materials have been developed by a traditional solid-state reaction method. Preparation of phosphors through this method need very high temperatures and offers irregular morphologies with different particle sizes and shapes, which is due to the heavy grinding and firing of raw materials in the preparation processes. From the last few years, many solution-based wet-chemical synthesis methods like solvothermal, hydrothermal, citrate-based sol-gel, co-precipitation, combustion and spray pyrolysis were developed to minimize the limitations from the solid-state method. Among the above several methods, synthesis of phosphors by a citrate-based sol-gel method has received great attention because of its benefits such as high degree of homogeneity, invariable ceramic powder with good purity, uniform morphology, low sintering temperature and efficient luminescent properties.

In this work, we report the citrate-based sol-gel synthesis of novel inorganic $Na_3Gd(VO_4)_2$ (NGVO):RE^{3+} ($RE^{3+} = Eu^{3+}$ or Dy^{3+} or Sm^{3+}) single doped phosphor materials. The morphology, phase formation and functional groups of all the phosphors were investigated by field-emission scanning electron microscope (FE-SEM) images, X-ray diffraction (XRD) patterns and Fourier transform infrared (FTIR) spectra, respectively. Photoluminescence (PL) properties of the NGVO:RE^{3+} ($RE^{3+} = Eu^{3+}$ or Dy^{3+} or Sm^{3+}) phosphors for different concentrations were studied under UV excitation wavelengths. The NGVO double vanadate host lattice material exhibited weak broadband blueish-green emission under UV excitation wavelengths. By controlling the RE^{3+} ions concentrations under their similar UV excitation wavelengths, the color tunable emissions from bluish green to yellow and red regions were completely absent, because of the week emission property of NGVO host lattice. Therefore, we mainly focused on the luminescent properties of the RE^{3+} ions activated NGVO phosphors and the involved luminescence quenching mechanism among them.

2. Experimental procedure

$Na_3Gd(VO_4)_2$ (NGVO) host lattice, $NG_{(1-x)}VO:xEu^{3+}$ ($x = 0.01$, 0.03, 0.05, 0.07, 0.09 and 0.11 mol), $NG_{(1-y)}VO:yDy^{3+}$ ($y = 0.005$, 0.01, 0.02, 0.03 and 0.04 mol) and $NG_{(1-z)}VO:zDy^{3+}$ ($z = 0.005$, 0.01, 0.02, 0.03 and 0.04 mol) phosphors were synthesized *via* a citric acid assisted sol-gel route. The raw materials such as sodium nitrate [$NaNO_3$ (99.0%)], gadolinium nitrate hexahydrate [($Gd(NO_3)_3\cdot6H_2O$) (99.9%)], ammonium metavanadate [NH_4VO_3 (99.96%)], europium nitrate pentahydrate [$Eu(NO_3)_3\cdot5H_2O$ (99.9%)], dysprosium nitrate hydrate [$Dy(NO_3)_3\cdot H_2O$ (99.9%)], samarium nitrate hexahydrate [$Sm(NO_3)_3\cdot6H_2O$ (99.9%)] and citric acid [$HOC(COOH)(CH_2COOH)_2$ (≥99.5%)] were purchased from Sigma-Aldrich Co., South Korea and used as received in the synthesis without any further purifications. Firstly, the stoichiometric amounts of sodium nitrate, gadolinium nitrate hexahydrate, europium nitrate pentahydrate, dysprosium nitrate hydrate, samarium nitrate hexahydrate and ammonium metavanadate were dissolved in 200 mL of de-ionized water and stirred for about 45 min. Later, 10 mol of citric acid (citric acid and metal ions ratio in the composition is 2:1) as a chelating agent was added and the stirring continued for another 1 h at room temperature. Afterwards, the solution was covered with a polyethylene cap and 80 °C of heat was applied through a hot plate for about 1 h under 500 rpm stirring, in order to attain the clear homogenous solution. During the heating process, the color of the solution turned into blue. The cap was removed after the progressive reaction time and the solution evaporated until a bluish wet-gel was obtained. The bluish wet-gel was dried in an oven at 100 °C for 24 h, thus producing porous solid matrices, which is so-called xerogel. The obtained xerogel was annealed at 400 °C for 4 h, which forms black colored flakes. Finally, it was calcined at different temperatures (600, 700 and 800 °C) for about 6 h to get pure phase form. The resultant transparent colored phosphor powder samples were further characterized by different characterization techniques.

The prepared powders of phosphors were characterized by the FE-SEM (Carl Zeiss Merlin), X-ray diffractometer (Mac Science M18XHF-SRA; Cu Ka = 1.5406 Å) and FTIR spectrophotometer (PerkinElmer Spectrum GX, Spectrophotometer; KBr pellet method). The PL properties of all phosphors were studied by using a fluorescence spectrometer (FluoroMate FS-2, Scinco; South Korea) and their temperature-dependent PL properties were also recorded by using the same fluorescence spectrometer (FluoroMate FS-2, Scinco; South Korea) equipped with a NOVA ST540 thermocouple. The lifetimes of the optimized phosphor samples were measured on a Photon Technology International (PTI, USA) phosphorimeter attachment to the main system with a Xe (25 W power) flash lamp.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the NGVO host lattice samples at different calcined temperatures of 600, 700 and 800 °C for 6 h after annealing the xerogel at 400 °C in a muffle furnace. At 600 °C, the NGVO host lattice showed the major diffraction peaks at two theta (2θ) degree positons of 14, 14.3, 17.3, 22.3, 28.6, 31, 32 and 33° with lower intensities. By increasing the temperature to 700 °C, all the diffraction peak intensities of the NGVO host lattice were significantly enhanced and this is a good sign for the improved crystallinity. All the XRD diffraction peaks obtained at 700 °C were ideally matched well with the standard JCPDs card# 49-1789, indicating a monoclinic structure with the space group of $P21/c$ (14). As the temperature increased to 800 °C, there were no significant changes in the monoclinic structure of the NGVO host lattice. The citric acid assisted sol-gel synthesis often exhibits characteristic diffraction peaks at relatively lower temperatures for the host lattice materials. However, the XRD patterns of the NGVO sample calcined at 700 °C were well crystallized with the monoclinic crystal structure and this temperature could be considered as the optimum temperature. The well-crystallized property of the host lattice was further confirmed by estimating the average crystallite sizes based on the familiar Scherrer formula ($D_{hkl} = k\lambda/\beta \cos\theta$) [19] to the XRD patterns of the host lattices at different calcination temperatures. Here, D is the average crystallite size, β is the full width at half maximum, θ is the corresponding diffraction angle at the wavelength λ (1.5406 Å) and k (0.9) represents the shape factor. Consequently, the estimated average crystallite or grain sizes for the prepared NGVO host lattice samples at different calcination temperatures of 600, 700 and 800 °C were 102.4, 138.5 and 111.9 nm, respectively. Fig. 1(b) shows the XRD patterns of the optimized NGVO:Eu^{3+}, NGVO:Dy^{3+} and NGVO:Sm^{3+} phosphors after 700 °C of calcination. From Fig. 1(b), it is clear that all the XRD