

White Light Generation from Single Gallium Oxide Nanoparticles co-doped with Rare-Earth Metals

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(Received August 25, 2014, Revised September 24, 2014, Accepted September 24, 2014)

The synthesis of pure and rare-earth doped gallium oxide (β -Ga₂O₃) nanoparticles is reported. The synthesized nanoparticles are characterized with XRD, TEM, and PL analyses. Strong blue emission is observed from un-doped gallium oxide nanoparticles, while nanoparticles doped with Eu³⁺ and Tb³⁺ give strong red and green emissions, respectively. When doped with Eu³⁺ and Tb³⁺ together, gallium oxide nanoparticles emit white light. The CIE co-ordinate of the emitted light was found to be (0.33, 0.33), which is well within the white light region.

Keywords : Nanoparticles, Gallium oxide, Terbium, Europium, White color

1. Introduction

Gallium oxide (Ga₂O₃) is typically an insulator at room temperature with a large bandgap of ~ 4.9 eV. It can transform into an n-type semiconductor with the introduction of oxygen vacancies [1]. It exists in different polymorphic phases, such as rhombohedral α -, monoclinic β -, and the cubic γ - and δ -phases, and can often be obtained from gallium oxyhydroxides (GaO(OH)) by a simple dehydration process [2,3]. Like other oxides of group III metals, gallium oxide is widely used to create luminescence materials [4] and catalysts [5,6], and it has been investigated for application as a transparent conducting oxide, as a gas sensor, and for use in optoelectronic devices [7–9].

Nano-sized gallium oxides are expected to exhibit unique electronic and optical properties superior to

those of traditional bulk gallium oxide due to the increased oxygen vacancies, the large surface area/volume ratio, and possibly a quantum effect [10–12]. Various synthetic methods have been reported for nano-sized gallium oxide and gallium oxyhydroxide. Ristic et al. [13] synthesized gallium oxide nanoparticles from gallium isopropoxide [Ga(OC₃H₇)₃] by a sol-gel method. By means of the hydrolysis of gallium isopropoxide, nano-sized α -gallium oxyhydroxides were obtained and were then heat-treated at 500°C to form nano-sized gallium oxides with diameters of 10~20 nm. Hamada et al. [14] reported the formation of mono-dispersed spherical gallium oxyhydroxides with diameters of 100 nm by the hydrolysis of gallium sulfate at elevated temperatures. Avivi et al. [15] prepared scroll-like cylindrically layered gallium oxyhydroxides with a small amount of metallic Ga enclosed inside via a

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This paper was presented at IMCM 2014.

sonochemical reaction. Recently, Zhao et al. [16] reported the synthesis of micro-/nano-sized gallium oxyhydroxide particles with different sizes and morphologies prepared via a simple soft-chemistry route under varying hydrothermal conditions.

The optical properties of gallium oxide have been studied extensively in recent years, due mainly to its applicability as a host material for rare-earth metals (RE) and for its use in electroluminescent devices [17,18]. It is notable that nano-structured gallium oxides optically behave differently from the bulk form. Kim et al. reported that there is significant deviation of the emission spectra of Eu-doped gallium oxide nanostructures with regard to its bulk structures [19].

Here, we report the synthesis of un-doped and RE-doped gallium oxyhydroxide nanoparticles by a simple precipitation method using GaCl_3 and NaOH in methanol. The gallium oxyhydroxide is heat-treated at 500°C to form gallium oxide nanoparticles as small as 5 nm in size. The photoluminescence properties of RE-doped gallium oxide phosphors are investigated, and the generation of white light from Tb, Eu-co-doped gallium oxide phosphors is demonstrated. The calculated CIE coordinates of the white light generated were found to be (0.33, 0.33).

II. Experimental Section

Anhydrous GaCl_3 (99.99%), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%), and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) were purchased from Sigma-Aldrich and were used as received. NaOH and methanol (99.9%) were purchased from Daejung Chemical and were used as received. The crystalline phases were determined by the powder X-ray diffraction patterns (XRD, Bruker D8 Advance, $\text{Cu K}\alpha$ target ($\lambda=0.15406$ nm) and a nickel filter). The size and morphology were characterized by means of transmission electron microscopy (TEM, FEI Tecnai G2, acceleration voltage=200 kV). The photoluminescence (PL) spectra were

collected using a Hitachi F-7000 spectrophotometer. The excitation light was from a Xe lamp with a monochromator, and the source powder was adjusted by changing the PMT voltage. All spectra in this paper were measured with a PMT voltage of 400 V, excitation and emission slits of 5.0 nm and a scan speed of 1,200 nm/min.

In a typical experiment, 0.01-x mol of GaCl_3 was dissolved in 100 ml of methanol. For Tb and Eu doping, x mol of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was added to this solution to make the total metal content 0.01 mol. A second solution was prepared by dissolving 0.03 mol of NaOH in 150 ml of methanol. The chloride solution was then added to the NaOH solution in a dropwise manner over a period of 0.5 hr. The resulting mixture was then stirred vigorously for 4 hr. The precipitate was collected by centrifugation, washed with methanol twice, and air-dried overnight. The dried precipitate was ground to a fine powder and annealed at 500°C for 4 hr under ambient conditions. The resulting white powder was characterized by XRD, TEM and PL.

III. Results and Discussion

The XRD pattern of the synthesized gallium oxide is shown in Fig. 1. The peaks are well matched with JCPDS file No. 41-1103 (monoclinic $\beta\text{-Ga}_2\text{O}_3$). The broad peaks of the XRD pattern indicate the formation of nanocrystals. The lattice parameter and size of the nanoparticles as calculated from the XRD data using Scherrer's formula are around 4~5 nm. No significant differences were observed in the XRD patterns of the doped and undoped gallium oxide nanoparticles. A TEM image of the synthesized nanoparticles is shown in Fig. 2. The size of the nanoparticles as calculated from the TEM images is ~5 nm, which is in good agreement with the size calculated from the XRD pattern.

Photoluminescence data pertaining to Tb-doped gallium oxide nanoparticles with various percentages

is shown in Fig. 3. It was found that the Tb emission was strongest with a 0.5% doping level and that it decreased with higher doping percentages. It was also found that when the Tb-doping level was as low as 0.001%, the blue emission by host defects was dominant, whereas when the level was raised ten times to 0.01%, both green emission by Tb and blue emission by the host could be detected, as shown in the inset of Fig. 3. The photoluminescence result of the Eu-doped gallium oxides showed the maximum red intensity level at a much higher percentage, i.e., 2.5% doping, as shown in Fig. 4. Similar to the Tb-doped gallium oxide, when the Eu-doping level was as low as 0.05%, the blue emission by host defects became dominant,

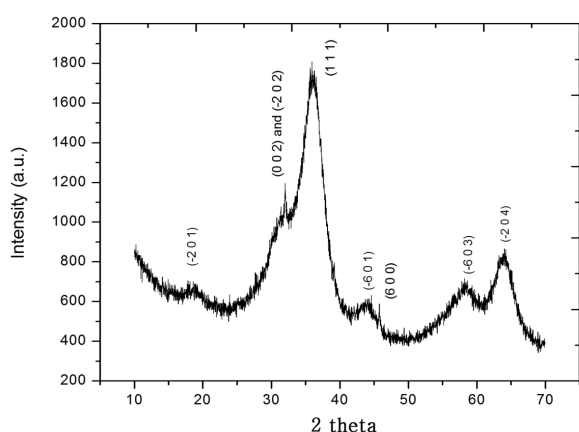


Figure 1. XRD pattern of gallium oxide nanoparticles (indexed for monoclinic β - Ga_2O_3).

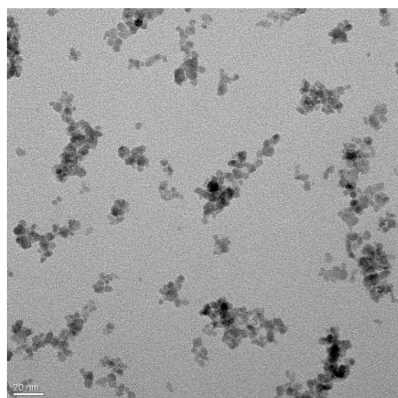


Figure 2. TEM image of gallium oxide nanoparticles.

but when the level was raised to 0.10%, the blue emission by the host was decreased but the red emission by Eu was increased, as shown in the inset of Fig. 4. These shifts from blue emission to green or red indicate that an energy transfer from the host defect to the doped Tb or Eu takes place.

As demonstrated in Figs. 3 and 4, when the Tb and Eu doping levels are carefully controlled, not only green and red color, but also blue color from the host defect can be observed at the same time. Therefore, to generate white light by RGB (red, green, blue) color from gallium oxide nanoparticles, the Tb and Eu dop-

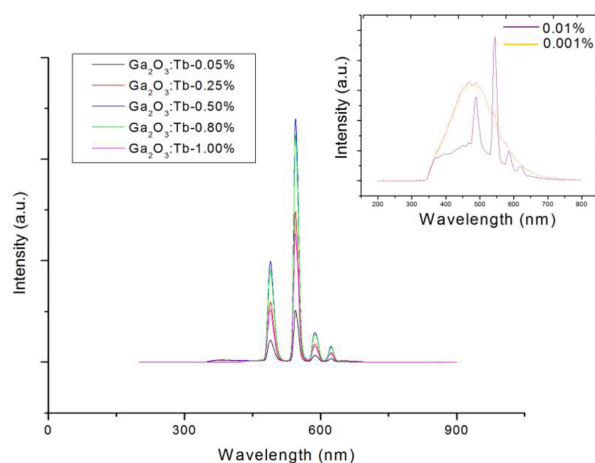


Figure 3. PL data of Tb^{3+} -doped gallium oxide nanoparticles under excitation of 365 nm.

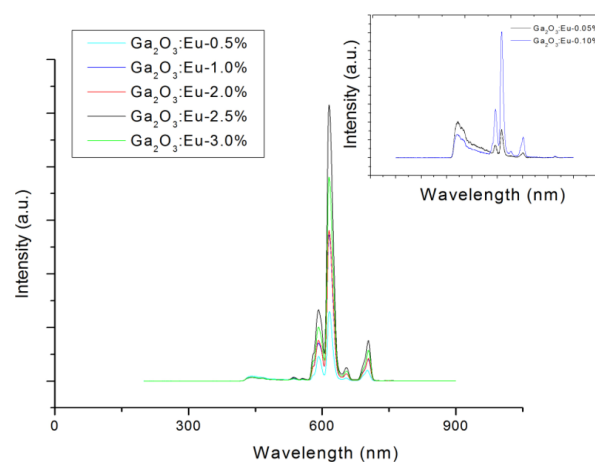


Figure 4. PL data for Eu^{3+} -doped gallium oxide nanoparticles under excitation of 365 nm.

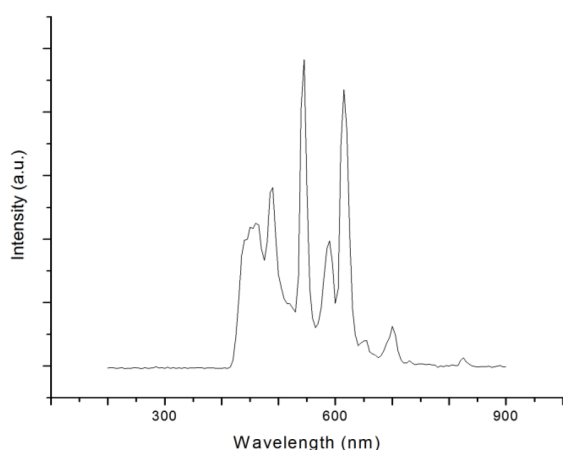


Figure 5. PL data of Tb and Eu co-doped gallium oxide nanoparticles under excitation of 365 nm.

ing amounts were adjusted so that they were low enough to allow the blue emission by the host to contribute. Therefore, both the Tb and Eu doping percentages were held under 0.01%. The photoluminescence result of gallium oxide nanoparticles co-doped with 0.004% Tb and 0.07% Eu is shown in Fig. 5. When excited at 365 nm, they exhibited emission throughout the visible range from 400 nm to 700 nm. The chromaticity coordinates were assigned to (0.33, 0.33), which falls well in the white region of the 1931 Commission Internationale de L'Eclairage (CIE) chromaticity diagram, as indicated in Fig. 6.

IV. Conclusion

By a simple precipitation method and calcination step, gallium oxide nanoparticles with an average size of 4~5 nm were successfully synthesized. Pure gallium oxide powder was found to emit strong blue light, which is attributed to its high population of defects due to its nano-size with high capillarity. Green and red emissions induced from the respective doped Tb and Eu were counterbalanced in a corresponding single powder by controlling the doping level against blue emission by host defects. Controlled the co-doping of

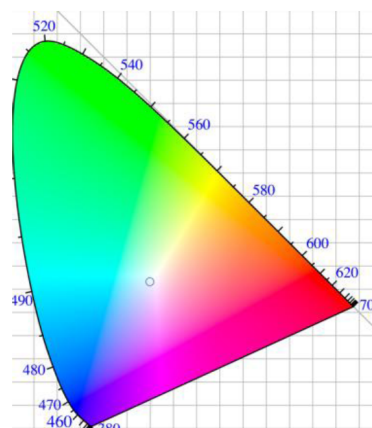


Figure 6. CIE coordinates of white light by Tb and Eu co-doped gallium oxide nanoparticles, as indicated by the circle.

Tb and Eu into the gallium oxide host enabled the single powder to generate white light, of which the color coordinates fall well into the CIE white region. The chromaticity of the emitted light could be controlled by controlling the relative doping levels of Tb and Eu as well as total doping levels of Tb and Eu. The present result can simplify the device structures of white LEDs by replacing two or three types of phosphors with a Tb/Eu co-doped gallium oxide phosphor. In addition, this co-doped phosphor can provide great advantages to control the chromaticity of phosphors by merely varying the internal chemical composition in the single powder.

Acknowledgements

This work was supported by the internal programs of the Korea Institute of Science and Technology (Proj. No. 2E24571).

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