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Investigation of the Luminescence Properties of Dy^{3+} doped $Lu_3Ga_2Al_3O_{12}$ Phosphors for X-ray Imaging and White LEDs

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In this research, Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor was synthesized by using the combustion method with a solid state reaction at 1500 °C for 12 hours in a furnace. Host materials such as Lu_2O_3, Ga_2O_3, Al_2O_3 and activator such as Dy_2O_3 were used. The crystal structure and the lattice constants were confirmed by using X-ray diffraction. The emission spectrum of the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor under excitations by UV light and X-rays showed peaks at 482 nm, 580 nm, 670 nm and 760 nm due to electron transitions from the $^4F_{9/2}$ to the ^6H_j orbited. The $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor emits blue, green-yellow and red light when excited by UV light and X-rays. The CIE chromaticity diagram for the emission spectrum gives a color close to white, which indicates that Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor may be a good material for use in a light-emitting diode. The $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor has a high sensitivity to X-rays and gamma rays because of its high Z-number ($Z_{\rm eff} = 57$) and density. Therefore, the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor can be applied for X-ray imaging in medical fields.

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I. INTRODUCTION

Lanthanide-based phosphors have recently become attractive because of their wide range of applications, including LEDs, lasers, medical imaging and non-destructive inspection, in various industrial fields [1–3]. Especially, the white LED has received much attention. In 1996, a white LED using a yellow-light-emitting $Y_3Al_5O_{12}$:Ce^{3+} phosphor mounted on a blue LED chip was developed and commercialized as the first known blue-YAG white [6]. Presently, many phosphors are being developed for a white LED using a yellow, red or green phosphor mounted on a blue LED chip to improve its white color property [6]. In this study, a Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor was fabricated as a new material for X-ray imaging in medical fields because of its having a strong X-ray absorption due to its high Z-number ($Z_{\rm eff} = 57$) [1–3]. The strong absorption can reduce radiation exposure to the subject. Therefore, rare-earth-based phosphors have received much attention from researchers [1–3]. The Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor emits lights in the wavelength range from 470 to 600 nm (blue, green-yellow and red light) due to transitions from the $^4F_{9/2}$ orbital to the ^6H_j orbital [3]. The white color combined with blue, green-yellow and red lights can be applied in LEDs. The $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor shows a charge transfer excitation at wavelengths below 250 nm. The allowed transitions due to the charge transfer of Dy^{3+} ion from the ground $4f$ state to the excited $5d$ state result in a broadband excitation in the region near 200 nm. The f-d transitions result in a fast decay as parity and spin are allowed [4–6]. The other sharp excitation peaks from 250 nm to 500 nm belong to the $4f$-$4f$ transitions of Dy^{3+} ions. The f-f transitions result in a slow decay due to parity and spin being forbidden [4–6]. In the present research, a Dy^{3+} doped $Lu_3Ga_2Al_3O_{12}$ phosphor was fabricated for the first time as far as we know. To confirm the f-f and the f-d transitions, we investigated the emission spectra cause by exposure to UV or X-ray radiation and the decay time.

II. EXPERIMENTAL

The Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor was fabricated by using a solid-state reaction. The starting ma-

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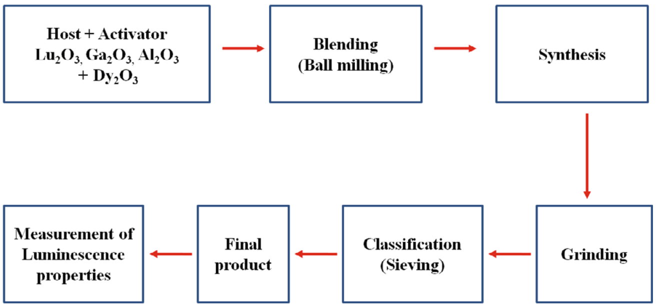

Fig. 1. Diagram for the fabrication and the measurement of the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor.

terials were used according to the following chemical reaction:

$$1.5Lu_2O_3 + Ga_2O_3 + 1.5Al_2O_3 + 1mol\%Dy_2O_3 \rightarrow Lu_3Ga_2Al_3O_{12} : Dy^{3+}$$

The above starting materials were ball milled and sintered at 1500 °C for 12 hours. The phosphor was then synthesized using a horizontal electric furnace, after which it was cooled to room temperature at a rate of 100 °C/h. The experimental process for the synthesis of the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor is shown in Fig. 1. An X-ray diffraction (XRD) measurement (Panalytical X'Pert Pro, UK) was used to confirm the crystalline structure of the sintered phosphor. The system was operated at 40 kV and 30 mA, and measurements were made over the 2 theta range from 10° to 70°. The speed and the size of the scan were 0.02°/s and 0.02° [7]. The result of the XRD measurement of the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor was compared with JCPDS card PDF #46-0448 ($Gd_3Ga_2Al_3O_{12}$) [5]. A spectro-fluorometer (Fluorolog-3) using 450-W xenon light was used to confirm the photoluminescence spectra and decay time. The X-ray excited radioluminescence spectrum was measured by using an X-ray generator (65 kV, 1 mA) and a spectrophotometer (Ocean Optics QE 65000 spectrometer, USA).

III. RESULTS

The patterns for the 1-mol% Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor and for JCPDS card number of #046-0448 ($Gd_3Ga_2Al_3O_{12}$) are shown in Fig. 2 [5]. The results show that the Miller indices (h, k, l) coincide with the JCPDS values. The $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor was successfully synthesized by using combustion method because all peaks are well matched with JCPDS values and no extra peaks were observed at room temperature or below.

The photoluminescence spectrum of the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor is shown in Fig. 3. The emission spectrum due to UV light is caused by energy transitions from the $^4F_{9/2}$ orbital to the ^6H_j orbital.

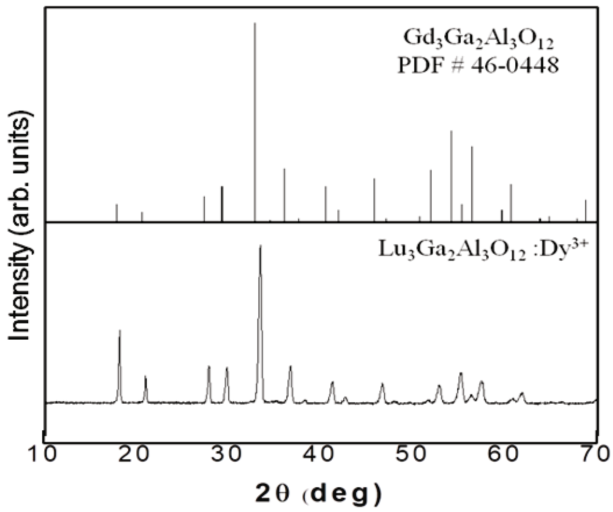

Fig. 2. XRD patterns of the standard PDF card of #46-0448 for $Gd_3Ga_2Al_3O_{12}$ (top) and the synthesized Dy^{3+} doped $Lu_3Ga_2Al_3O_{12}$ phosphor (bottom).

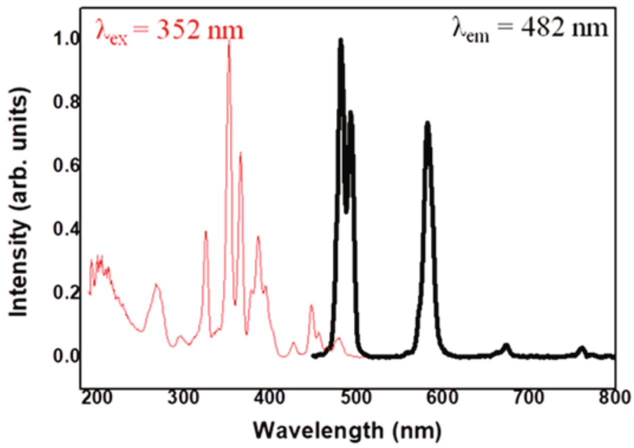

Fig. 3. Excitation (red line) and emission (black bold line) spectra for the Dy^{3+} doped $Lu_3Ga_2Al_3O_{12}$ phosphor exposed to UV light.

Emission peaks were observed at 482 nm, 580 nm, 670 nm, and 760 nm [8–10]. The excitation spectrum due to UV light contains peaks associated with the $^6H_{15/2}$ to $^4K_{11/2}$, $^4D_{7/2}$, $^4M_{17/2}$, $^6P_{7/2}$+$^4M_{15/2}$, $^4I_{11/2}$+$^6P_{5/2}$, $^4I_{13/2}$+$^4K_{7/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ excitations [8–10]. A charge transfer band (CTB) is seen at a wavelength show near 200 nm due to the $O^{2-} \rightarrow Dy^{3+}$ transition through the $4f$ state to the $5d$ state allowed transition [11–14].

Figure 4 shows a schematic energy-level diagram for the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor. The emission spectrum of $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor is due to electron transitions from the $^4F_{9/2}$ to the ^6H_j orbital. The emission peaks were observed at 482 nm ($^4F_{9/2}$ to $^6H_{15/2}$), 580 nm ($^4F_{9/2}$ to $^6H_{13/2}$), 670 nm ($^4F_{9/2}$ to $^6H_{11/2}$) and 760 nm ($^4F_{9/2}$ to $^6H_{9/2}$) respectively [11–

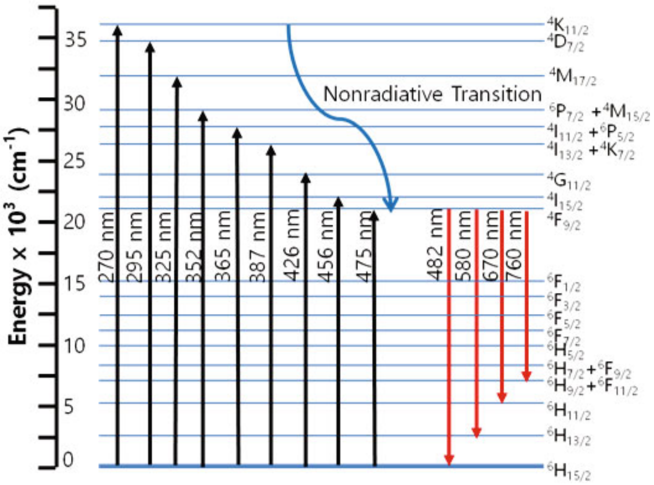

Fig. 4. Schematic energy-level diagram of the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor and the excitation (black lines in upward direction) and emission (red lines in downward direction) lines.

14]. The excitation spectrum of the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor due to UV light contained peaks associated with the $^6H_{15/2}$ to $^4K_{11/2}$ (270 nm), $^4D_{7/2}$ (295 nm), $^4M_{17/2}$ (325 nm), $^6P_{7/2}+^4M_{15/2}$ (352 nm), $^4I_{11/2}+^6P_{5/2}$ (365 nm), $^4I_{13/2}+^4K_{7/2}$ (387 nm), $^4G_{11/2}$ (426 nm), $^4I_{15/2}$ (456 nm) and $^4F_{9/2}$ (475 nm) transitions [11–14]. In the case of the *f*-*f* transition, unlike the *f*-*d* transitions the spectral shape is less dependent on host materials. Dy^{3+}-doped phosphors show similar spectral shapes, as can be seen in Fig. 3 [11–14]. The emission spectrum for the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor excited by UV light matched well the emission spectrum for the phosphor excited by X-rays. The Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor emits blue, green-yellow and red light when excited by either UV light or X-rays [11–14].

The emission spectrum of the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor excited by X-rays is shown in Fig. 5. The emission peaks were observed at 482 nm ($^4F_{9/2}$ to $^6H_{15/2}$), 580 nm ($^4F_{9/2}$ to $^6H_{13/2}$), 670, 684 nm ($^4F_{9/2}$ to $^6H_{11/2}$) and 760 nm ($^4F_{9/2}$ to $^6H_{9/2}$) [8]. The emission wavelengths of the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor caused by X-rays matched its photoluminescence well [8].

Figure 6 shows the decay time of the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor for emission at 589 nm when excited by 352 nm UV light. The decay curve was fitted to an exponential function, as shown in Fig. 6. The function is given by $y = A_1^* \exp^{(-x/t1)} + y_0$ [5], where y is the phosphorescence intensity at time x, A_1 is a constant, and t_1 is the lifetime for exponential component [5]. Using the above relation, the decay time of the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor was measured as ~0.65 ms.

Figure 7 shows the CIE (Commission International de I'Eclairage) chromaticity diagram considering the emission spectrum for the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor under excitation by 352 nm UV light. The evaluated X and Y values of the CIE chromaticity diagram are 0.321 and 0.368, respectively. The diagram for the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor shows a combined emission color of white due the peaks in the blue, green-yellow and red regions.

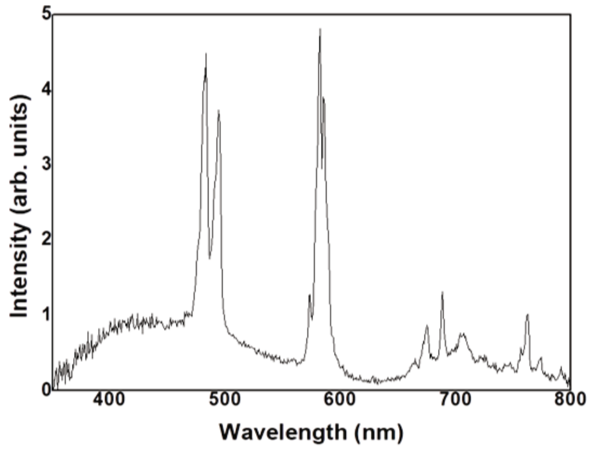

Fig. 5. Emission spectrum for the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor when exposed to X-rays.

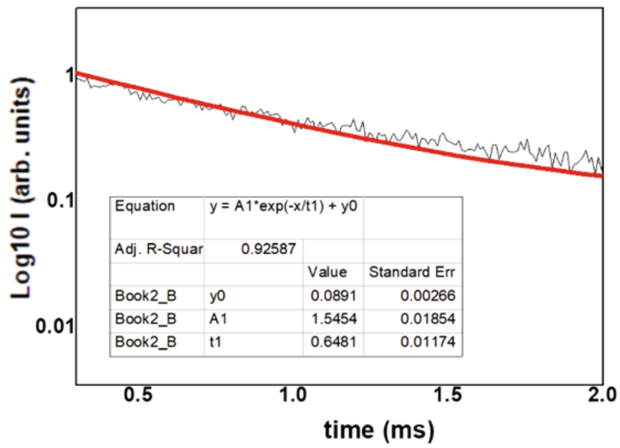

Fig. 6. Decay time of the Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor excited by using UV light, calculated by fitting with an exponential function (red colored line).

IV. CONCLUSIONS

The Dy^{3+}-doped $Lu_3Ga_2Al_3O_{12}$ phosphor was fabricated by using a solid-state reaction method in an electric furnace. To confirm the crystal structure and the lattice constants, we measured the X-ray diffraction (XRD) patterns. The XRD measurement result was confirmed by comparing it with JCPDS card number of #046-0448 ($Gd_3Ga_2Al_3O_{12}$). The Miller indices (h, k, l) coincide with the JCPDS numbers. The luminescence spectrum from the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor excited by X-

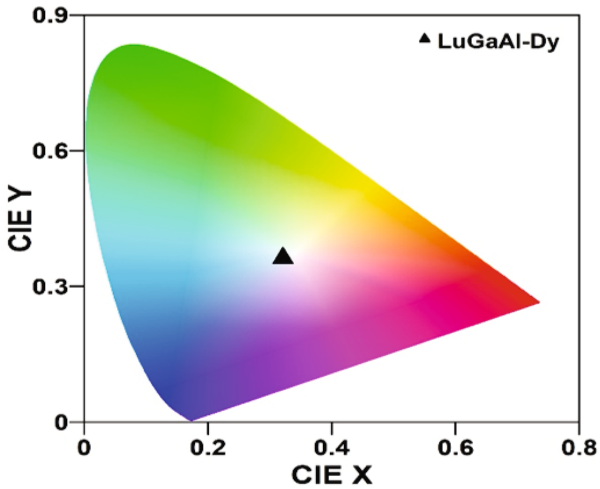

Fig. 7. CIE chromaticity diagram for the Dy^{3+} doped $Lu_3Ga_2Al_3O_{12}$ phosphor.

rays matched well the photoluminescence spectrum from the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor. The luminescence spectra from $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} excited by X-rays and UV light were observed to have peaks at 482 nm ($^4F_{9/2}$ to $^6H_{15/2}$), 580 nm ($^4F_{9/2}$ to $^6H_{13/2}$), 670 nm ($^4F_{9/2}$ to $^6H_{11/2}$) and 760 nm ($^4F_{9/2}$ to $^6H_{9/2}$) [11–14]. The $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor emits a white color combined with blue, green-yellow and red light when excited by UV light and X-rays [8]. The white color indicates that it can be applied in LEDs. The phosphorescence decay time of $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} was found to be $\sim$0.65 ms. The $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor has high sensitivities to X-rays and gamma-rays because of its high Z-number ($Z_{\text{eff}} = 57$) and density [5]. Therefore, the $Lu_3Ga_2Al_3O_{12}$:Dy^{3+} phosphor is a very promising material for applications in medical fields for X-ray imaging.

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