Photoluminescence and cathodoluminescence properties of Li^+ doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$

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Li^+ -doped cubic $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ phosphors were synthesized at 1200°C in air by co-precipitation (CP) and solid state reaction (SS) methods. X-ray diffraction analysis revealed that, regardless of synthetic method, the average crystallite size for Li^+ -free $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ was approximately 400 nm, then increased with the amount of Li^+ and at 20 mol %, reached about 2.3 μm . Under excitation of the charge transfer band of Eu^{3+} at 245 nm, $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ exhibited a dominant photoluminescence (PL) red emission peak at 611 nm assigned to the electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} . The red emission peak intensity increased consistently with the amount of Li^+ -doping, while CP method was found to be effective in improving the red emission intensity at lower amounts of Li^+ -doping from 0 to 8 mol %. Cathodoluminescence (CL) property was studied by mounting the synthesized phosphor on a vacuum fluorescent display (VFD) operated at an anode voltage of 50 V. The $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ exhibited a similar spectrum with an intense red emission peak at 611 nm, and the highest luminance intensity for the CL red emission was achieved for 8 mol % Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by SS method. The evaluation results of PL and CL properties suggested that, besides the crystallite size of $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$, dispersion property of Eu^{3+} ions in the host Gd_2O_3 was an important factor for improving luminescent properties of $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$. Moreover, under the present VFD operating condition at the low excitation voltage, it was thought to be essential for improving CL emission intensity to maintain a sufficient surface area of $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$.

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1. Introduction

Field Emission Displays (FEDs) have been widely used for televisions, personal computers and cell phones in our daily life to replace the conventional cathode ray tube (CRT) displays.¹⁾ In the past decades, most of the interest has been focused on the materials for FEDs operating at low electron beam excitation voltages (≤ 10 kV).²⁾ However, under the low excitation voltages, there is no ideal material with sufficient brightness, fast response and long term stability used for the modern luminescence devices.³⁾ Former researches have mainly used sulfide red phosphors such as $\text{Y}_2\text{O}_2\text{S:Eu}^{3+}$, $\text{SrGa}_2\text{S}_4\text{:Eu}^{3+}$, ZnS:Ag,Cl , $(\text{Zn/Cd})\text{S:Cu}$ etc.⁴⁾⁻⁷⁾ Unfortunately, the sulfide phosphors are unstable under electron bombarding in vacuum, which leads to the chemical degradation of phosphor layers and emit sulfide-containing gases under the operation condition.^{3),8)} On the other hand, due to the sharp lines, high efficiency and stability in high vacuum, rare-earth sesquioxides have received increased attention and their luminescence properties have been investigated.⁹⁾⁻¹¹⁾ Europium(III)-doped Gd_2O_3 phosphor ($\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$) is one of the attractive red emitting rare-earth sesquioxide phosphors with potential applications in various lighting and

display devices.¹²⁾ Both Gd_2O_3 and Eu_2O_3 have three different kinds of cubic, monoclinic and hexagonal phases. It is reported that the smaller electronegativity of Gd^{3+} permits an easier charge transfer from the $2p$ orbital of O^{2-} to the $4f$ orbital of Eu^{3+} , and the ${}^8S \rightarrow {}^6D$ and ${}^8S_{7/2} \rightarrow {}^6I_J$ transitions of Gd^{3+} overlap in the charge transfer band (CTB), which leads to efficient energy transfer from Gd^{3+} to Eu^{3+} in $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$. Therefore, cubic $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$ exhibits stronger and red-shift CTB of the charge transfer edge, which allows sharper red emission at 611 nm than the monoclinic $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$.^{13),14)}

However, compared with commercial red phosphors like $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S:Ag}^+$ and $\text{Y}_2\text{O}_2\text{S:Eu}^{3+}$,²⁾ the red emission intensity of $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$ is not sufficient for practical applications. There are two main approaches to improve the luminescence properties of $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$: morphology and/or structure controlling, and with hetero-element ions. Several $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$ phosphors like nanotubes,¹⁵⁾ nanowires,¹⁶⁾ and nanospherical particles¹⁷⁾ have been synthesized. However, during synthesis of the nanometer-sized $\text{Gd}_{2-x}\text{Eu}_x\text{O}_3$, lots of chemical reagents like urea and dispersant are used, which introduces impurity ions and leads to form non-radiation centers. For the second approach, alkali metal ions are useful dopants to enhance the emission intensity because of the flux effect and the formation of oxygen vacancies.^{2),18)-22)} Moreover, due to the radius smaller than the Gd^{3+} , Li^+ is an attractive secondary dopant (compare with the Na^+ and K^+) for

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host Gd₂O₃, which contributes to increase local distortion of the crystal field surrounding the Eu³⁺ activator.²³⁾ In our previous study on Gd_{2-x}Eu_xO₃ with optimized Eu³⁺ concentration of 12 mol % (Gd_{1.88}Eu_{0.12}O₃), the PL red emission intensity was found to increase approximately three times by Li⁺-doping at 12 to 16 mol %. Moreover, the thermal stability of the cubic Gd_{1.88}Eu_{0.12}O₃ was significantly improved by the Li⁺-doping, and even after annealing for 72 h at 1300°C, which exceeds the cubic/monoclinic phase transformation temperature, the relative fraction of the cubic phase in the 12 mol % Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ was measured to be 90%.²³⁾

As a part of our study on luminescent properties, here we report a comparative study of PL and cathodoluminescence (CL) properties of Li⁺-doped cubic Gd_{1.88}Eu_{0.12}O₃. In the present work, Gd₂O₃-Eu₂O₃ mixed powder was prepared by using co-precipitation technique and cubic Gd_{1.88}Eu_{0.12}O₃ phosphors with different amounts of Li⁺ were synthesized by heat treatment at 1200°C in air for 3 h. PL properties were evaluated by using a conventional spectrophotometer, while CL emission properties under low excitation voltage were investigated by mounting the synthesized Gd_{1.88}Eu_{0.12}O₃ phosphor on a vacuum fluorescent display (VFD). The resulting PL and CL properties were discussed by comparison with those synthesized by the conventional solid solution method.

2. Experimental procedures

2.1 Synthesis of Li⁺-doped cubic Gd_{1.88}Eu_{0.12}O₃ phosphors

Gadolinium oxide (Gd₂O₃), europium oxide (Eu₂O₃) and lithium carbonate (Li₂CO₃) were used as starting powders. All the powders were purchased from Mitsuwa Chemical Company, Japan (99.99% purity). Appropriate amounts of Gd₂O₃ and Eu₂O₃ were completely dissolved in a HNO₃ aqueous solution with *pH* = 1. Through the whole process, the aqueous solution was stirred by a magnetic stirrer. The precipitation was carried out by adding aqueous NH₄OH solution until the solution reached a *pH* of 8. The precipitate was separated by filtration and dried at 100°C for 3 h. The dried powder was calcined at 1200°C in air for 3 h. In a typical synthesis, a proper amount of the calcined powder was mixed with Li₂CO₃ as a source of Li⁺ from 0 to 20 mol % [Li⁺mol% = Li⁺mol/(Gd³⁺mol + Eu³⁺mol)]. Then, the mixed powder (about 2 g) was stirred with 5 ml ethanol for 10 min and subsequently placed into a drying furnace at 100°C for 5 min to remove the ethanol. The dried powder was heat-treated at 1200°C in air for 3 h.

To study the effect of synthesis method on luminescence properties, Li⁺-doped cubic Gd_{1.88}Eu_{0.12}O₃ phosphors were also synthesized by conventional solid solution method.^{19),23)} Appropriate amounts of Gd₂O₃ and Eu₂O₃ were mixed with Li₂CO₃ and ethanol followed by stirring in the same manner shown above. After drying in a furnace at 100°C, the mixed powder was heat-treated at 1200°C in air for 3 h.

2.2 Characterizations

Room temperature X-ray diffraction (XRD; X'pert Pro α 1, Philips) analysis was performed on the 1200°C heat-treated samples using Cu K α radiation (λ = 0.15405 nm). The average crystallite size of Gd_{1.88}Eu_{0.12}O₃ phosphors was evaluated by the Scherrer equation:^{24),25)}

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

where D is the average crystallite size, λ is the X-ray wavelength (λ = 0.15405 nm), B is the full width at half maximum of the observed peak, and the factor of 0.9 for spherical objects was used in this study.

Morphology and microstructure of Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ phosphors was observed using a scanning electron microscope (SEM, JSN-6360LV, JEOL) at 25 kV acceleration voltages.

PL excitation and emission spectra were record by a spectrophotometer (F-7000, Hitachi) with a 150 W Xenon lamp as the excitation source. CL emission properties of the synthesized Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ phosphors were studied by mounting the phosphor on a VFD operated at an anode voltage of 50 VDC (Pulse Width of 100 msec. and Pulse Duty of 1/60 generated by FC110, YOKOGAWA, Japan) with an average current density of 1.3 mA/cm². The CL emission spectrum and the luminance intensity at room temperature were recorded and measured, respectively by a spectroradiometer (TOPCON SR-3A, Topcon Technohouse Corporation, Japan). This VFD mount test was performed at Noritake Itron Corporation, Japan.

3. Result and discussion

3.1 Crystalline phase and morphology

Powder XRD patterns for 1200°C-synthesized Gd_{1.88}Eu_{0.12}O₃ synthesized by co-precipitation (CP) and solid solution (SS) methods are shown in Fig. 1. The diffraction peaks detected for each sample were identical to those for the standard powder diffraction file for cubic Gd₂O₃ (JCPDS No. 86-2477, space group: *Ia-3*). Even for the samples with 20 mol % Li⁺, no

Fig. 1. XRD patterns for Gd_{1.88}Eu_{0.12}O₃ doped with different amounts of Li⁺ synthesized by CP and SS methods after heat treatment at 1200°C in air for 3 h (indicates cubic Gd₂O₃).

Fig. 2. Average crystallite size for $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ doped with different amounts of Li^+ synthesized by CP and SS methods after heat treatment at 1200°C in air for 3 h.

Fig. 4. Variation of specific surface area (SSA) for $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ doped with different amounts of Li^+ synthesized by CP and SS methods.

Fig. 3. SEM images of $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ doped with different amounts of Li^+ synthesized by heat treatment at 1200°C in air for 3 h (CP and SS indicate CP method and SS method, respectively).

additional crystalline phases containing Li^+ species were detected.

Figure 2 shows the average crystallite size for $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ doped with different amounts of Li^+ synthesized by SS and CP methods, and typical SEM images of the $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ are shown in **Fig. 3**. At all the amount of Li^+ -doping from 0 to 20 mol %, the average crystallite size for the $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by CP method was close to that synthesized by SS method. The average crystallite size monotonously increased with increasing the amount of Li^+ -doping. Finally at 20 mol %, the average crystallite size reached approximately 2.3 μm .

The morphologies of the Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by CP method were similar to those synthesized by SS method. The Li^+ -free sample was composed of round-shaped grains with several hundred nanometers in size. With increasing amount of Li^+ -doping, the grain size increased and the neck growth at the grain boundaries became apparent. This microstructure coarsening could be due to the flux effect which promoted liquid phase-assisted sintering for minimizing the surface free energy of cubic $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ grains (Fig. 3).

The degree of microstructural coarsening was further evaluated by measuring the specific surface area (SSA) of the $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$. The SSA values were plotted as a function of amount of Li^+ -doping and are shown in **Fig. 4**. The SSA for the Li^+ -free $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by SS method was 2.230 m^2/g , then decreased with increasing amount of Li^+ doping. At the 20 mol % Li^+ -doping, SSA became as low as 0.254 m^2/g .

The samples synthesized by CP method also showed the same tendency. However, at the Li^+ doping from 0 to 8 mol %, the SSA for $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by CP method was apparently lower than that by SS method. Above 8 mol %, SSA values were lower than 0.4 m^2/g and compatible with those synthesized by SS method.

3.2 PL properties

Figure 5 demonstrates PL excitation spectrum ($\lambda_{\text{em.}} = 611 \text{ nm}$) and emission spectrum ($\lambda_{\text{ex.}} = 245 \text{ nm}$) for 12 mol % Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by CP method. The spectra were well consistent with those synthesized by SS method in our previous study²³⁾ and the excitation spectrum exhibits three main peaks at 245, 255 and 277 nm. The highest peak at 245 nm is attributed to the charge transfer band (CTB) between O^{2-} and Eu^{3+} .^{13),14)} The peaks at 255 and 277 nm superimposed on the CTB of Eu^{3+} are due to the Gd_2O_3 host excitation, and are assigned to the $^8S \rightarrow ^6D$ and $^8S \rightarrow ^6I$ transitions of Gd^{3+} , respectively. The weak peak at 311 nm can be assigned to the $^8S \rightarrow ^6P$ transition of Gd^{3+} . The peaks in the excitation spectrum indicate the energy transfer from Gd_2O_3 and Gd^{3+} to the doped Eu^{3+} . On the other hand, the several weak peaks at 350–400 nm are due to the direct excitation of the Eu^{3+} ground state into the higher level of the $4f$ orbital.¹⁹⁾

Upon an excitation at 245 nm, typical $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions of Eu^{3+} at 580, 591, 611 and 628 nm are observed in the PL emission spectrum. The weak emission peak at 580 nm

can be assigned to the $^5D_0 \rightarrow ^7F_0$ transition and the emission peak at 591 nm is attributed to the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition. The most intense emission peak at 611 nm and another weak peak at 628 nm are due to the $^5D_0 \rightarrow ^7F_2$ electric dipole transition.

Typical PL emission spectra ($\lambda_{\text{ex}} = 245$ nm) for the Gd_{1.88}Eu_{0.12}O₃ phosphors synthesized in this study are shown in Fig. 6. There was a tendency for the dominant red emission peak intensity at 611 nm to increase consistently with the amount of Li⁺-doping. Then, the values of the peak intensity at 611 nm for the Gd_{1.88}Eu_{0.12}O₃ phosphors were plotted and analyzed. As shown in Fig. 7(a), the intensity for the phosphor synthesized by SS method increased with increasing amount of Li⁺-doping and reached a maximum at 20 mol % Li⁺-doping. On the other hand, the intensity for the Li⁺-free Gd_{1.88}Eu_{0.12}O₃ synthesized by CP method was high and compatible with that achieved for the 16 mol % Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ synthesized by SS method. Then, the intensity increased slightly to reach a maximum at 8 to 20 mol %, and was close to that for the 20 mol % Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ synthesized by SS method.

The dominant emission peak at 611 nm due to the $^5D_0 \rightarrow ^7F_2$ electric dipole transition is hypersensitive to the symmetry of local environment around Eu³⁺ ion,²⁶ while that due to the $^5D_0 \rightarrow ^7F_1$ transition at 591 nm is attributed to a magnetic dipole transition, which is not affected by the inverse site symmetry. It is well known that the relative intensities of the $^5D_0 \rightarrow ^7F_1$ and

Fig. 5. PL excitation and emission spectra for 12 mol % Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ synthesized by CP method.

Fig. 6. PL emission spectra ($\lambda_{\text{ex}} = 245$ nm) for Gd_{1.88}Eu_{0.12}O₃ phosphors doped with different amounts of Li⁺ synthesized by CP and SS methods.

$^5D_0 \rightarrow ^7F_2$ emissions strongly depend on the local symmetry of Eu³⁺, and the $^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ emission intensity ratio (asymmetry ratio) indicates the degree of distortion from the inversion symmetry of the local environment around Eu³⁺ ion in the host lattice.²⁷ In our previous study on Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ synthesized by SS method,²³ it was experimentally demonstrated that the dominant PL red emission peak intensity at 611 nm was proportional to the asymmetric ratio, and the asymmetric ratio increased consistently with the amount of Li⁺-doping. Then, the asymmetric ratios were evaluated for the phosphors synthesized by CP method. The values were plotted as a function of amount of Li⁺-doping and compared with those synthesized by SS method. As shown in Fig. 7(b), the asymmetric ratio increased with the amount of Li⁺-doping, however at

Fig. 7. PL emission properties of Gd_{1.88}Eu_{0.12}O₃ as a function of amount of Li⁺-doping: (a) Dominant red emission intensity at 611 nm under UV excitation at 245 nm and (b) asymmetry ratio.

Fig. 8. CL emission spectrum under VFD operating condition at an acceleration voltage of 50 V for 8 mol% Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by SS method.

all the amount of Li^+ -doping in the range of 0 to 20 mol%, the asymmetric ratio for $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by CP method was found to be lower than that synthesized by SS method.

Generally, large surface area carries large number of defects into the host lattice. Defects have a serious drawback in PL emission intensity since they provide non-radiative recombination routes for the electrons and holes. If the defect density is sufficiently reduced by crystallite growth, PL emission intensity would be improved.^{20),28)–30)} In the present study, PL red emission intensity for the $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by SS method was successfully enhanced by host Gd_2O_3 crystallite growth via liquid phase-assist sintering. However, as shown in Figs. 2 and 3, the Li^+ -free $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by CP method exhibited a fine-grained microstructure with an average crystallite size of approximately 400 nm. One possible reason for the high PL emission intensity is due to the improved dispersion property of Eu^{3+} ions doped in the host Gd_2O_3 . During the synthesis process using co-precipitation technique, Gd_2O_3 and Eu_2O_3 were converted to $\text{Gd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$, respectively. The resulting soluble salts could be well and uniformly mixed at the molecular level, which leading to minimize the energy trapped by the non-radiative recombination center during the energy migration process between one Eu^{3+} ion to another one caused by segregation of Eu^{3+} ions in the host Gd_2O_3 . As a result, relatively high PL emission intensity was thought to be achieved for the $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ at the Li^+ -doping from 0 to 8 mol%.

3.3 CL properties

The Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ was mounted on a VFD, and under the VFD operating condition at an anode voltage of 50 V, CL properties were studied. As a typical result, Fig. 8 presents a CL emission spectrum for 8 mol% Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by SS method. Characteristic emission peaks due to the $f-f$ transition of Eu^{3+} ions are observed. The dominant emission peak is located at 611 nm assigned to the $^5D_0 \rightarrow ^7F_2$ electric dipole transition of Eu^{3+} . Thus, the $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ exhibits intense CL red emission under the VFD operating condition in this study.

Figure 9(a) shows luminance intensity evaluated for the dominant CL red emission of Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$. In contrast to the liner relation between the amount of Li^+ and PL emission intensity shown in Fig. 7(a), Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by SS method exhibited a maximum luminance

Fig. 9. CL emission properties of $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ doped with different amounts of Li^+ synthesized by CP and SS methods: (a) Luminance intensity evaluated for the dominant CL red emission at 611 nm as a function of amount of Li^+ -doping, and (b) Relation between SSA and luminance intensity for $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ phosphors investigated in this study (Numbers in parentheses indicate the amount of Li^+ doping).

intensity at 8 mol% Li^+ , while above this amount, the intensity decreased with the amount of Li^+ . On the other hand, when $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ was synthesized by CP method, the initial luminance intensity (at 0 mol% Li^+) remarkably improved to 31.3 cd/m^2 , and the intensity achieved a maximum at 4 mol% Li^+ . However, this intensity (37.3 cd/m^2) was apparently lower than that achieved for the 8 mol% Li^+ -doped $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ synthesized by SS method (53.9 cd/m^2).

Figure 9(b) demonstrates relation between the SSA and the luminance intensity for $\text{Gd}_{1.88}\text{Eu}_{0.12}\text{O}_3$ phosphors investigated in this study. Regardless of synthesis method, the luminance intensity reaches a maximum at around 0.8 m^2/g , while below this value, the intensity decreases with increasing amount of Li^+ -doping.

At electron beam excitation voltages ranging from 1 to 10 kV, the penetration depth of electrons into the solid is well described by Feldman³¹⁾ using the high-energy excitation model. Based on the model, for example, Liu et al. reported that the electron penetration depth at 5 kV for rare-earth cation-doped SrIn_2O_4 was estimated as 67.44 nm.³²⁾ At high excitation voltages, CL properties should be governed by material factors such as crystallinity of host material and dispersion property of activator ions in the host lattice. On the other hand, under our present VFD operating condition at an anode voltage of 50 V, the electron penetration depth must be extremely shallow. Therefore, it is

essentially required for enhancing the luminance intensity to maintain a sufficient surface area of a phosphor mounted in a VFD. In this study, crystallinity of Gd_{1.88}Eu_{0.12}O₃ and dispersion property of Eu³⁺ in the host lattice could be improved in association with decreasing surface area of Gd_{1.88}Eu_{0.12}O₃. Thus, the SSA value of 0.8 m²/g is considered as an approximate lower limit that can offer possibilities for enhancing luminance intensity.

4. Summary

In this study, Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ phosphors were synthesized at 1200°C in air by co-precipitation (CP) and solid solution (SS) methods. The PL and CL properties of the synthesized phosphors were studied and discussed based on the material factors in terms of the average crystallite size, dispersion property of Eu³⁺ ions in the host Gd₂O₃ and specific surface area (SSA). The results are summarized as follows:

- (1) The average crystallite size for Gd_{1.88}Eu_{0.12}O₃ synthesized by CP method was closed to that synthesized by SS method at all the amount of Li⁺-doping from 0 to 20 mol %. The average crystallite size at 0 mol % Li⁺ was approximately 400 nm, then increased consistently with amount of Li⁺-doping. The maximum average crystallite size achieved at 20 mol % Li⁺ was about 2.3 μm.
- (2) Under the excitation of charge transfer band between O²⁻ and Eu³⁺ at 245 nm, Gd_{1.88}Eu_{0.12}O₃ exhibited a dominant red emission peak at 611 nm attributed to the ⁵D₀→⁷F₂ electric dipole transition, and the intensity of the dominant red emission peak increased consistently with the average crystallite size of Gd_{1.88}Eu_{0.12}O₃.
- (3) The dispersion property of Eu³⁺ ions doped in the host Gd₂O₃ was thought to be improved by using CP method, which could lead to the relatively high PL red emission intensity achieved for the Gd_{1.88}Eu_{0.12}O₃ at the Li⁺ doping from 0 to 8 mol %.
- (4) The Li⁺-doped cubic Gd_{1.88}Eu_{0.12}O₃ phosphor mounted on a VFD showed room-temperature red CL at an anode voltage of 50 V, and the maximum luminance intensity for the CL red emission was achieved for 8 mol % Li⁺-doped Gd_{1.88}Eu_{0.12}O₃ synthesized by SS method.
- (5) Under the present VFD operation condition at the low excitation voltage, the penetration depth of electrons into the Gd_{1.88}Eu_{0.12}O₃ was considered to be extremely shallow. Therefore, it could be essential for enhancing the luminance intensity to maintain a sufficient surface area of the Gd_{1.88}Eu_{0.12}O₃ mounted on a VFD. As a result, the SSA value of approximately 0.8 m²/g was suggested as a lower limit required for improving CL emission intensity.

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