Luminescence Properties of Dy^{3+}- (or Tm^{3+}-) Doped Ga_2O_3 and $ZnGa_2O_4$ Phosphors

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Dy^{3+}- (or Tm^{3+}-) doped Ga_2O_3 and $ZnGa_2O_4$ phosphors were prepared using the solid state reaction method to investigate their photoluminescent characteristics. Under 254 nm excitation, Dy^{3+}-doped Ga_2O_3 exhibited two emission bands of 460~505 nm and 570~600 nm. On the other hand, Dy^{3+}- (or Tm^{3+}-) doped $ZnGa_2O_4$ phosphors exhibited a broad-band emission extending from 330 nm to 610 nm, peaking at about 430 nm (or 370 nm). In this study, an emission peak shift of nearly 50 nm towards longer wavelength region was observed with Dy^{3+} doping in the $ZnGa_2O_4$.

Key words : Dysprosium, Thulium, Gallium oxide, Zinc gallate, Luminescence

I. Introduction

Gallium oxide, Ga_2O_3, is a thermally and chemically stable material, which is insulating at room temperature but semiconducting at higher temperature. The stable, low-temperature (α) form has the α-corundum crystal structure, in which the oxygen ions form a hexagonal close-packed array and all of the Ga^{3+} ions are in octahedral coordination. However, above approximately 600°C, α-Ga_2O_3 transforms to β-Ga_2O_3, which has the monoclinic crystal structure with the optical bandgap of 4.6 eV. Because of its optical and electrical properties, Ga_2O_3 has found applications in metal-insulator structures on GaAs and facet coatings for GaAs-based laser.[1]

Zinc gallate, $ZnGa_2O_4$, has the spinel crystal structure and its optical bandgap is 4.4 eV. $ZnGa_2O_4$ is known to be a self-activated phosphor that has a blue emission band under excitation by both UV and low-voltage electrons.[2,3] In addition, $ZnGa_2O_4$ shows emission from green to red when it is doped with Mn or Cr.[4,5] $ZnGa_2O_4$ phosphors show the excellent stability under high temperature operation and good cathodoluminescent characteristics at low voltage excitation. Due to these attractive advantages of $ZnGa_2O_4$, it has been known to be a good candidate material for applying displays by low-voltage electron excitation, such as FED (Field Emission Display) and VFD (Vacuum Fluorescence Display).

In recent years, an interest in Dy^{3+}-activated phosphors has been showing because of its two dominant emission bands in the yellow region (570~600 nm) and blue region (460~505 nm).[6] The yellow band corresponds to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ ($\Delta L=2$; $\Delta J=2$) and the blue band corresponds to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition. In addition, phosphor materials doped with Tm^{3+} have attracted much attention because of its blue luminescence.[7,8]

In this study the photoluminescent properties of Dy^{3+}- (or Tm^{3+}-) doped Ga_2O_3 and $ZnGa_2O_4$ phosphors prepared by a solid-state reaction method are presented. The concentration dependence of dopants and the effect of reduction treatment in relation to the concentration quenching and activation effects were studied to improve the blue emission spectra of doped Ga_2O_3 and $ZnGa_2O_4$.

II. Experimental Procedure

The schematic diagram of the sample preparation of Dy^{3+}-(or Tm^{3+}-) doped Ga_2O_3 and $ZnGa_2O_4$ phosphors by the solid-state reaction is shown in Fig. 1. Starting materials used in the preparation of $ZnGa_2O_4$ phosphor and doping materials were highly pure powders of ZnO (99.999%), Ga_2O_3 (99.999%), Tm_2O_3 (99.9%), and Dy_2O_3 (99.9%), which were from High Purity Chemicals Laboratory Co., Ltd., Japan. These materials were thoroughly mixed according to the stoichiometric ratio of the target phosphors with acetone using mortar and pestle, and allowed to dry. The mixtures were sintered at 1200°C for 3 hours in air. The sintered powders were fired under a reducing atmosphere of 98%N_2-2%H_2 at 900°C for 1 hour.

The analysis of the crystal structure of the powder samples was made by the X-ray diffraction (XRD) method using $CuK\alpha$ radiation (Ni filter). The binding energies of each compound of $ZnGa_2O_4$ were measured by VG ESCALAB Mark II photoelectron spectrometer (XPS) using $AlK\alpha$ radiation. The photoluminescence (PL) emission and excitation spectra of powder samples were obtained using a Perkin-Elmer LS50 luminescence spectrometer. Up to 0.3 g of a powder sample was placed in a circular cell holder with a fused silica window. Powder
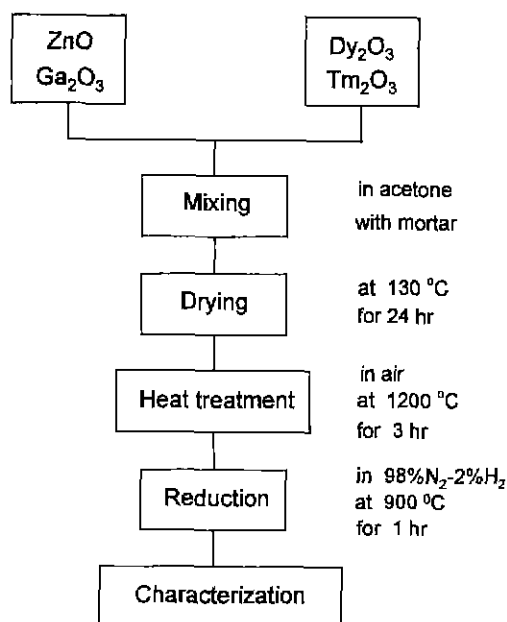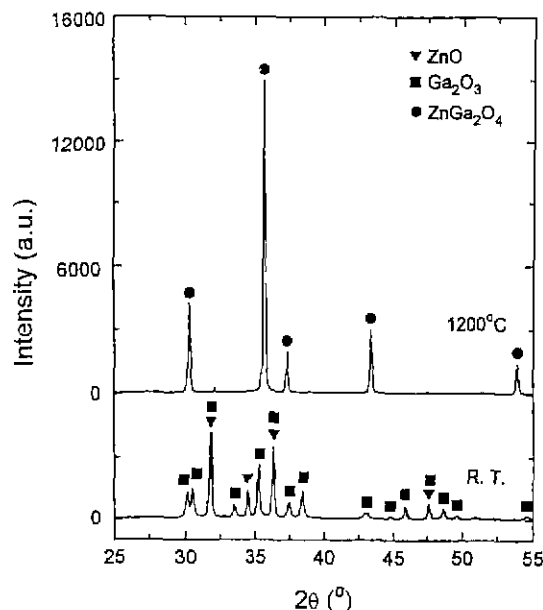
Fig. 1. Schematic diagram of the sample preparation of Dy^{3+}- (or Tm^{3+}-) doped Ga$_2$O$_3$ and ZnGa$_2$O$_4$ phosphors by a solid state reaction method.

Fig. 2. X-ray diffraction patterns of raw mixtures and sintered body of ZnO-Ga$_2$O$_3$ powders heated 1200°C for 3 hours in air.

samples were excited with 254 nm radiation from a pulsed xenon discharged lamp. The emission wavelength was scanned from 300 nm to 600 nm at a scanning rate of 480 nm/min. For the measurements of excitation spectra, the excitation wavelength was scanned from 230 nm to 400 nm at the identical scanning rate, and monitored at the emission wavelength of 450 nm.
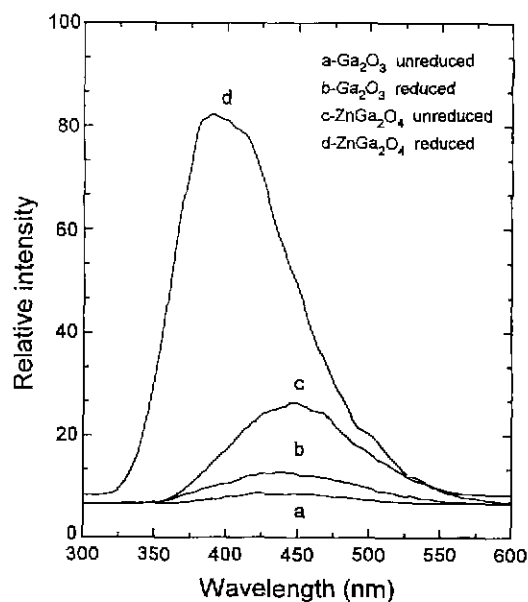
III. Results and Discussion

Figure 2 shows the X-ray diffraction patterns of the raw mixture and the sintered body of ZnO-Ga$_2$O$_3$ powders heated at 1200°C for 3 hours in air. As can be seen from this figure, Ga$_2$O$_3$ in the raw mixture showed the X-ray diffraction patterns of β-phase which has the monoclinic crystal structure. On the other hand, it was seen that ZnGa$_2$O$_4$ spinel phase could be successfully obtained in the sintered powder. This result agrees well with the X-ray diffraction patterns of ZnGa$_2$O$_4$ reported by Itoh.[9] The spinel structure can be represented by the formula AB$_2$O$_4$, where A and B are the metal ions filling the tetrahedral and the octahedral interstices, respectively. The ZnGa$_2$O$_4$ spinel is a normal spinel with all of the Zn^{2+} ions in A sites, Ga^{3+} ions in B sites, and with the lattice constant a$_0$=8.37Å.

Figure 3 shows the effect of reduction treatment on emission spectra of Ga$_2$O$_3$ and ZnGa$_2$O$_4$. Under 254 nm excitation, sintered powder of Ga$_2$O$_3$ at 1200°C for 3 hours in air showed a very weak and broad-band emission spectrum, extending from 330 nm to 580 nm, with a peak at about 450 nm. High temperature heat treatments of Ga$_2$O$_3$ cause to form vacancies. These vacancies were in-

Fig. 3. Effect of reduction treatment on emission spectra of Ga$_2$O$_3$ and ZnGa$_2$O$_4$

troduced in sufficient concentration into the Ga$_2$O$_3$ lattice to disrupt the continuity and serve as energy traps and, subsequently, emission centers to develop luminescence. According to mild reduction of the sintered powder of Ga$_2$O$_3$ at 900°C for 1 hour under a 98%N$_2$-2%H$_2$ atmosphere, the emission intensity slightly increased (Fig. 3-b). The reason for this is that mild reduction introduces semiconducting characteristics. Semiconduction was attributed to the presence of a lot of vacancies. On the other hand, the sintered powder of ZnGa$_2$O$_4$ showed a broad-band emission spectrum, extending from 330 nm

to 580 nm, with a peak at 450 nm and a maximum half band with about 100 nm. The main peak centered at 450 nm comes from $^4T_2 \rightarrow {}^4A_2$ transitions.[2] This wavelength is located within the blue light range. $ZnGa_2O_4$ showed a tremendous increase in the emission intensity by reduction treatment. The main peak of spectrum of the sintered $ZnGa_2O_4$ powder shown in Fig. 3-d shifted from 450 nm to 380 nm by mild reduction treatment.

The compositional dependence of the luminescence of $ZnGa_2O_4$ was empirically analyzed to identify the cation-anion group in the activated spinel host lattice responsible for emission. $ZnGa_2O_4$, ZnO, and Ga_2O_3 were sintered separately, first in air at 1200°C for 3 hours, followed by reduction treatment at 900°C for 1 hour under a 98%N_2-2%H_2 atmosphere. The excitation spectra of ZnO and Ga_2O_3 were obtained and compared to the excitation spectrum of $ZnGa_2O_4$ to attempt to determine if luminescence resulted from Zn-O, Zn-Ga, or Ga-O interactions. The emission wavelength was monitored at 450 nm and the excitation wavelength scanned from 230 nm to 400 nm, as shown in Fig. 4. As can be seen from this figure, the excitation spectrum of Ga_2O_3 is most similar to that of $ZnGa_2O_4$, which exhibits a peak at 245 nm. Therefore, gallium may be responsible for the luminescence of $ZnGa_2O_4$. Optical absorption spectrum obtained from our semiconducting Ga_2O_3 samples was in good agreement with the results of Tippins.[10]

XPS analysis provides to investigate the stoichiometric consideration and the binding energy for $ZnGa_2O_4$ phosphor. The XP spectrum of $ZnGa_2O_4$ after reducing treatment is shown in Fig. 5. From the quantitative analysis of this powder, the atomic ratio of Zn to Ga was 1.32 to 2.50. This value was vary close to the stoichiometric value of $ZnGa_2O_4$. The result shows that the volatiliza-
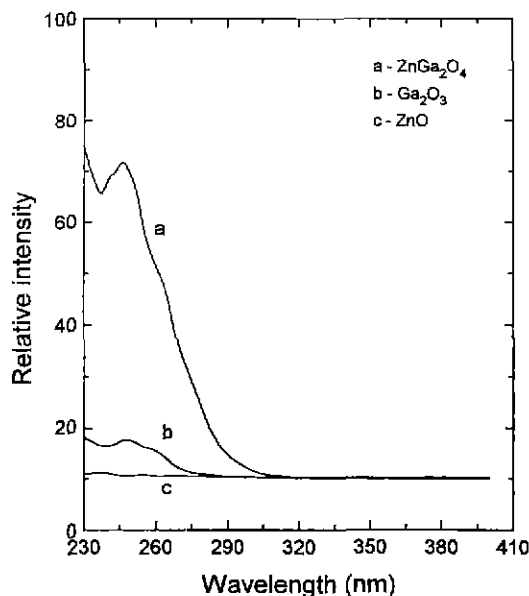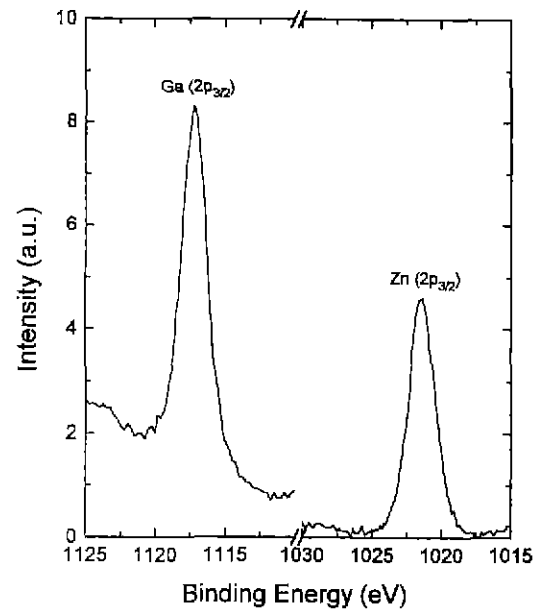

Fig. 5. XP spectrum of $ZnGa_2O_4$ after reducing treatment.

tion of Zn and Ga was nearly occurred by sintering and reduction treatment used in this study. No other impurities were detected in this XPS analysis. On the other hand, the measured binding energies for the Zn ($2p_{3/2}$), Ga ($2p_{3/2}$), and Ga (3d) signal peaks of $ZnGa_2O_4$ were 1021 35 eV, 1117.25 eV, and 19.50 eV, respectively. The binding energy of Ga (3d) in the $ZnGa_2O_4$ phosphor nearly corresponded to that of given literature data,[11] indicating that gallium is present as Ga^{3+} in the Ga_2O_3.

Figure 6 shows the emission spectra of Ga_2O_3 as a function of Dy^{3+} concentration. As can be seen from this figure, the photoluminescence of Dy^{3+}-doped Ga_2O_3 was dominated by the two groups of emission lines at 460~505 nm (the blue band) and 570~600 nm (the yellow band). The emission bands of 460~505 nm and 570~600 nm apparently
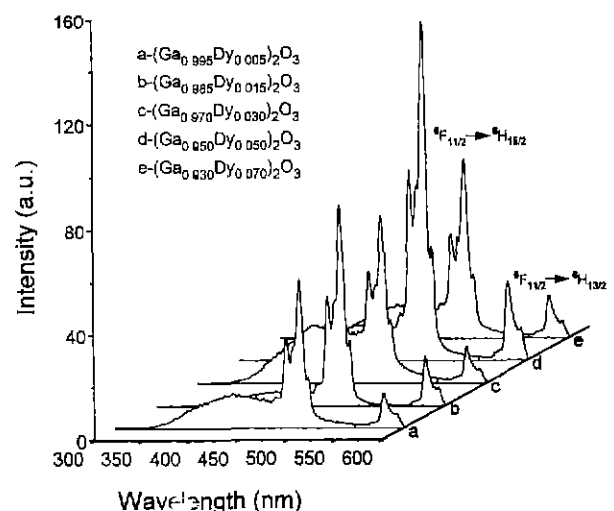

Fig. 4. Excitation spectra of ZnO, Ga_2O_3, and $ZnGa_2O_4$ monitored at 450 nm.

Fig. 6. Emission spectra of Ga_2O_3 as a function of Dy^{3+} concentration.
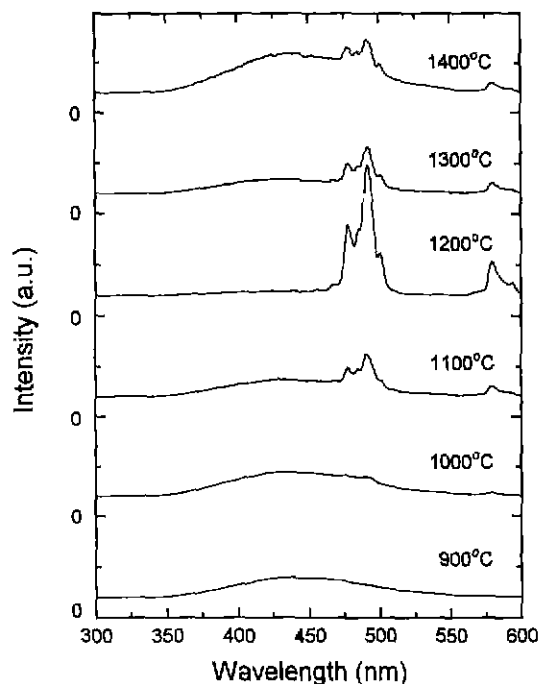
Fig. 7. Emission spectra of 0.050% mol Dy^{3+}-doped Ga$_2$O$_3$ as a function of sintering temperature.

Fig. 8. Emission spectra of ZnGa$_2$O$_4$ as a function of Dy^{3+} concentration.

Fig. 9. Emission spectra of ZnGa$_2$O$_4$ as a function of Tm^{3+} concentration.

arise from $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^6H_{13/2}$ transitions, respectively. On the other hand, the emission band under about 460 nm was not luminescent characteristics due to Dy^{3+} doping ion but self-activated luminescence of Ga$_2$O$_3$. As shown in Fig. 6-d, the maximum emission intensity was obtained at 0. 050 mole% Dy^{3+}-doped Ga$_2$O$_3$.

The intensity of the photoluminescence varies considerably depending on temperature, duration of heat treatment, and reducing condition. In addition, the luminescence appears to be very sensitive to the small amount of impurities. For example, emission spectra of 0.050% mol Dy^{3+}-doped Ga$_2$O$_3$ fired from 900°C to 1400°C for 3 hours in air were shown in Fig. 7. As can be seen from this figure, the sample fired at 1200°C showed clearly the two groups of emission bands at 460~505 nm and at 570~600 nm, raised from $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^6H_{13/2}$ transitions, respectively.

Figure 8 shows the emission spectra of ZnGa$_2$O$_4$ as a function of Dy^{3+} concentration. As can be seen from this figure, the spectra of 0.003~0.010% mol Dy^{3+}-doped ZnGa$_2$O$_4$ showed the maximum emission intensities, peaking at about 430 nm. It shows a shift of nearly 50 nm towards longer wavelength region, as compared with undoped ZnGa$_2$O$_4$ with a peak at about 380 nm. After that, the emission intensity of Dy^{3+}-doped ZnGa$_2$O$_4$ gradually decreased with increase of Dy^{3+} concentration. The concentration quenching of Dy^{3+} luminescence usually occurred at over 0.015% mol concentration. An enriched quantity of rare earth frequently leads to a quenching phenomenon in luminescence owing to the energy transfer between rare earth ions, i.e. concentration quenching.
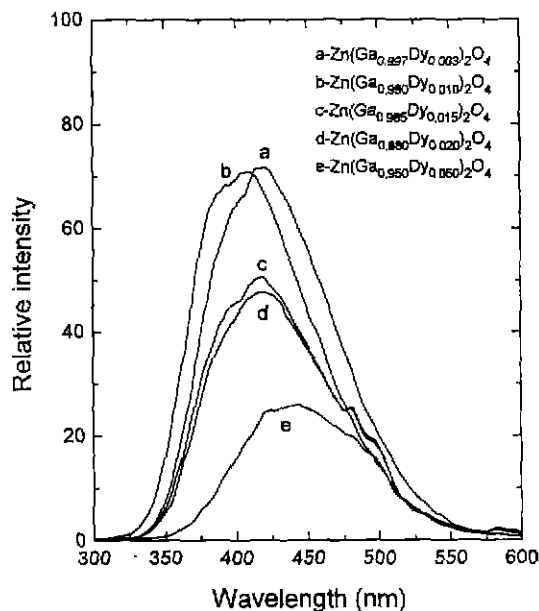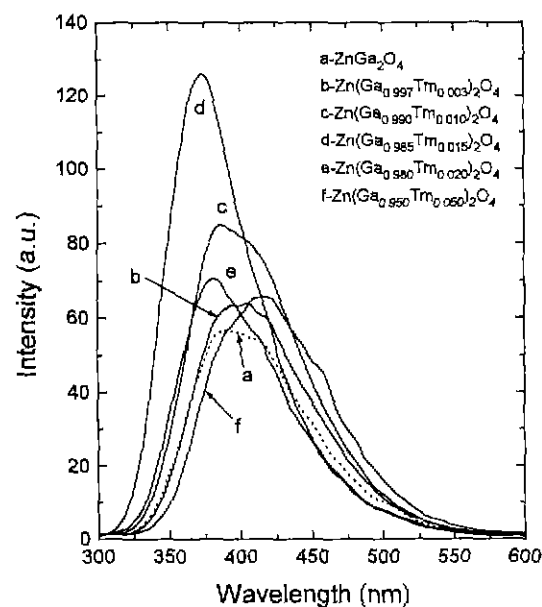
Figure 9 shows the emission spectra of ZnGa$_2$O$_4$ as a function of Tm^{3+} concentration. Tm^{3+}-doped ZnGa$_2$O$_4$ phosphor shows a broad-band emission spectrum, extending from 330 nm to 580 nm. After emission intensity showed an optimal level of dopant concentration in the ZnGa$_2$O$_4$ doped with 0.015% mol Tm^{3+} and a decrease of emission intensity was observed due to concentration quenching by dopants. The emission intensity of 0.015% mol Tm^{3+}-doped ZnGa$_2$O$_4$ was almost two times as much as that of undoped ZnGa$_2$O$_4$ and it also showed a slight shift towards shorter wavelength region with a peak at 370 nm.

IV. Conclusions

The luminescence properties of the Dy^{3+}-(or Tm^{3+}-) doped Ga_2O_3 and $ZnGa_2O_4$ phosphors prepared by a solid state reaction method were studied with the aids of mainly photoluminescence spectrometer XRD and XPS. The photoluminescence of self-activated $ZnGa_2O_4$ was occurred by Ga_2O_3, which is a similar type of excitation spectrum. The mild reduction treatment for the sintered samples caused an increase in the emission intensity. It was due to the formation of many vacancies in the host lattice during the mild reduction. The emission peak of Dy^{3+}-doped $ZnGa_2O_4$ shifted towards longer wavelength region at about 50 nm, as compared with undoped $ZnGa_2O_4$ with a peak at about 380 nm. On the other hand, the emission intensity of 0.015% mol Tm^{3+}-doped $ZnGa_2O_4$ is almost twice as much as that of undoped $ZnGa_2O_4$. Activated luminescence of Ga_2O_3 and $ZnGa_2O_4$ by dopants and reduction treatment may lead to the development of new and efficient photoluminescence materials.

Acknowledgment

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