A Study on the Preparation of ZnGa_2O_4 Phosphor and its Luminescence Properties*

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The ZnGa_2O_4 phosphors were prepared using the solid state reaction method to investigate their photoluminescence characteristics and luminescence mechanism. Under 254 nm excitation, the ZnGa_2O_4 phosphor exhibited a broad-band blue luminescence with an emission spectral peak at 450 nm. The reduction treatment of ZnGa_2O_4 phosphors in partial hydrogen atmosphere showed a tremendous increase of emission intensity of all phosphors. On the other hand, Mn^{2+} -doped ZnGa_2O_4 phosphor exhibited a strong narrow-band green luminescence with an emission spectral peak at 504 nm, and showed a maximum emission intensity at the Mn^{2+} concentration of 0.006 mol %.

KEY WORDS : Zinc Gallate, Manganese, Luminescence, Spinel Structure

1. Introduction

The ZnGa_2O_4 , zinc gallate, is a spinel compound with the unit cell belonging to the cubic space group O_h^7 (Fd3m) and its optical bandgap is 4.4 eV. The ZnGa_2O_4 is known to the self-activated phosphor that has the blue emission band under excitation by both UV and low voltage electrons¹⁾²⁾. In addition, the ZnGa_2O_4 shows emission from green to red when it is doped with Mn and Cr (or Co)³⁾⁴⁾. The ZnGa_2O_4 phosphors have been prepared by solid state reaction, sol-gel, radio frequency sputtering, and ion cluster beam method¹⁾⁵⁾.

The ZnGa_2O_4 phosphors show the excellent stability under high temperature operating life-time test and good cathodoluminescence characteristics at low voltage. Due to these attractive advantages of ZnGa_2O_4 , it is a good candidate material for applying display by low voltage electron excitation, such as FED (Field Emission Display) and VFD (Vacuum Fluorescence Display). Especially, the Mn^{2+} -doped ZnGa_2O_4 phosphors are known to be one of the best candidates for FED applications because of their stability to electron bombardment in high vacuum and long life-time over sulfide-based phosphors, such as $\text{ZnS} : \text{Cl}, \text{Al}$ and $(\text{Zn}, \text{Cd})\text{S} : \text{Ag}, \text{Cl}$ ⁶⁾. Although a number of studies have been made on the ZnGa_2O_4 phosphors, a little is known about their luminescence mechanism.

The purpose of this work is to establish the powder processing of ZnGa_2O_4 phosphors and to improve the photoluminescence properties of ZnGa_2O_4 phosphors.

2. Experimental Procedure

ZnGa_2O_4 phosphors were prepared by the solid state reaction method. Starting materials used in the preparation of

ZnGa_2O_4 and Mn^{2+} -doped ZnGa_2O_4 phosphors were highly pure powders of ZnO (5N), Ga_2O_3 (4N), and MnO (3N), which were High Purity Chemicals Laboratory Co., Ltd., Japan. The concentration of dopant Mn was ranged from 0 to 0.02 mol %. Prewedged materials were thoroughly mixed in acetone in agate mortar, and dried to 130 °C for about 2 hours to drive off the solvent. The samples were sintered at 1,200 °C for 3 hours in air atmosphere. The sintered powders were reduced at various experimental conditions to investigate the optimum parameter of reduction.

Crystal structure of the powder samples were examined by the X-ray diffraction (XRD) method using Cu $K\alpha$ radiation (Ni filter). The microstructure of powder samples was observed by scanning electron microscopy (SEM). Electron-spin resonance (ESR) measurements were performed to examine Mn substitution of Zn site using diphenylpicrylhydrazil (DPPH) as the internal standard. The photoluminescence (PL) emission and excitation spectra of powder samples were obtained using a Perkin-Elmer LS50 luminescence spectrometer. Each sample was loaded into a circular holder and excited with 254 nm radiation from a pulsed xenon discharged lamp. The emission spectra was scanned over the range of wavelengths from 300 to 600 nm. To measure the excitation spectra, analyzer monochromator was set to the maximum wavelength of the emission spectra and then an excitation monochromator was scanned over the range of wavelengths from 230 to 400 nm.

3. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the raw mixture and the sintered body of $\text{ZnO-Ga}_2\text{O}_3$ powders heated at 1,200 °C for 3 hours in air atmosphere. As can be seen from this figure, Ga_2O_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 only ZnGa_2O_4

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Fig. 1 X-ray diffraction patterns of raw mixture and sintered body of ZnO-Ga₂O₃ powders heated at 1,200 °C for 3 hours in air atmosphere.

spinel phase can be successfully obtained in the sintered powder. The result agrees well with the X-ray diffraction patterns of ZnGa₂O₄ reported by Itoh, et al.⁶⁾. The spinel structure can be represented by the formula AB₂O₄, where A and B are the metal ions filling the tetrahedral and the octahedral interstices, respectively. The ZnGa₂O₄ spinel is known to be almost perfectly normal ordered with the Zn²⁺ ions occupying the A sites and the Ga³⁺ ions occupying the B sites, and with the lattice constant $a_0 = 8.37 \text{ \AA}$.

Fig. 2 shows the scanning electron microphotographs of the powder mixtures: (a) raw powder mixture (ZnO, MnO, Ga₂O₃) at room temperature, (b) sintered powder sample ((Zn_{0.994}Mn_{0.006})Ga₂O₄) at 1,200 °C for 3 hours. As can be seen from these photographs, raw powders showed the irregular shape and their particle size was about 0.05 μm. Such fine

Fig. 2 Scanning electron microphotographs of the powder mixtures:

- (a) raw powder mixture (ZnO, MnO, Ga₂O₃).
(b) sintered powder sample ((Zn_{0.994}Mn_{0.006})Ga₂O₄).

Fig. 3 Effect of reduction temperature on intensity of luminescence of (Zn_{0.994}Mn_{0.006})Ga₂O₄.

particles changed to the size of about 0.5-2 μm by heat treatments. The ZnGa₂O₄ phosphors of sintered powders had a peach body color. However, the reduction treatment changed the color of samples to a white body color.

In order to examine the optimum experimental condition of reduction in 98 % N₂-2 % H₂ atmosphere with a flow rate of 20 ml/min, we investigated the degree of contribution of temperature to emission intensity. Fig. 3 shows the effect of reduction temperature on the intensity of luminescence of (Zn_{0.994}Mn_{0.006})Ga₂O₄. As shown in Fig. 3, the maximum emission intensity was obtained with a reduction temperature of 900 °C. Therefore, 900 °C was used as a reduction temperature in this work.

Fig. 4 shows the effect of reduction treatment on the emission spectra of ZnGa₂O₄. Under 254 nm excitation, the sintered powder of Ga₂O₃ at 1,200 °C for 3 hours in air atmosphere 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 treatment of Ga₂O₃ occurs to form vacancies. These vacancies were introduced in sufficient concentration into the Ga₂O₃ lattice to disrupt to develop luminescence. According to reducing the sintered powder of Ga₂O₃ at 900 °C for 1 hour in 98 % N₂-2 % H₂ atmosphere, the emission intensity slightly increased (Fig. 4-b). It is for this reason that mild reduction introduces semiconducting char-

Fig. 4 Effect of reduction treatment on emission spectra of Ga₂O₃ and ZnGa₂O₄.

Fig. 5 Emission spectra of Mn^{2+} -doped ZnGa_2O_4 with a function of Mn concentration.

acteristics. On the other hand, sintered powder of ZnGa_2O_4 showed a tremendous increase in the emission intensity by mild reduction treatment. This phenomenon is quite similar to that of $\text{ZnO}:\text{Zn}^{7)}$. Therefore, the increase of emission intensity of samples after reducing sintered powders may be explained by a result of the reduction Zn^{2+} to Zn^0 or formation of many vacancies. The main peak of spectrum of the sintered ZnGa_2O_4 powder shown in Fig. 4-d shifted from 450 nm to 380 nm by reduction treatment.

Fig. 5 shows the emission spectra of Mn^{2+} -doped ZnGa_2O_4 with a function of Mn concentration. Under 254 nm excitation, a broad-band blue emission extending from 330 nm to 580 nm in undoped ZnGa_2O_4 (Fig. 5-a) was observed. On the other hand, under the same excitation, the emission spectrum of Mn^{2+} -doped ZnGa_2O_4 phosphors exhibited a new strong narrow emission band with a peak at 504 nm, accompanying the quenching of blue emission of ZnGa_2O_4 . This wavelength is located within the green light range. The origin of green emission is attributed to the well-known ${}^4\text{G} \rightarrow {}^6\text{S}$ transition in the Mn^{2+} ion in $\text{ZnS}:\text{Mn}$ and the $\text{Zn}_2\text{SiO}_4:\text{Mn}$ phosphors⁸⁾. The green emission of this phosphor was caused by the for-

mation of Mn^{2+} in the host material of spinel-structure type under heat treatment. Green emission indicates that Mn^{2+} is in the four-coordinated position in the spinel structure lattice. The Mn^{2+} -doped ZnGa_2O_4 increased with the addition of Mn up to 0.006 mol %, but thereafter the value decreased with increasing the Mn concentration. The decrease of emission intensity for values greater than the critical concentration (Fig. 5-c) is mostly a result of concentration quenching. When the activator Mn concentration (Fig. 5-d, e) becomes too high, the probability of energy transfer exceeds the probability of emission. Therefore, excitation energy continually travels from one activator ion to another⁹⁾¹⁰⁾.

Fig. 6 shows the excitation spectra of $(\text{Zn}_{0.994}\text{Mn}_{0.006})\text{Ga}_2\text{O}_4$ and ZnGa_2O_4 monitored at 504 nm and 450 nm, respectively and scanned from 230 nm to 400 nm. As can be seen from this figure, the excitation spectrum of ZnGa_2O_4 monitored at 450 nm exhibited one absorption band with a peak at 254 nm. However, the excitation spectrum of $(\text{Zn}_{0.994}\text{Mn}_{0.006})\text{Ga}_2\text{O}_4$, monitored at 504 nm exhibited two absorption bands with peaks at 245 nm and 283 nm. The appearance of the 245 nm peak in the excitation spectra of $(\text{Zn}_{0.994}\text{Mn}_{0.006})\text{Ga}_2\text{O}_4$ suggests absorption of the excitation energy by the ZnGa_2O_4 host lattice. The host absorption band in the $(\text{Zn}_{0.994}\text{Mn}_{0.006})\text{Ga}_2\text{O}_4$ excitation spectrum indicates a high efficiency of energy transfer from host to Mn^{2+} ions¹¹⁾. The excitation energy is then transferred to and absorbed by the Mn^{2+} centers, as indicated by the peak at 283 nm and the subsequent increase in green luminescence. Mn^{2+} ions in the Mn^{2+} -doped ZnGa_2O_4 phosphors are acted as an activator sensitized emission²⁾.

In order to clarify the doping phenomena of ZnGa_2O_4 doped by Mn^{2+} ions, a measurement of ESR was carried out. Fig. 7 shows ESR spectra of the powder samples measured at room temperature: (a) raw powder mixture (ZnO , MnO , Ga_2O_3) at room temperature, (b) sintered powder sample $((\text{Zn}_{0.994}\text{Mn}_{0.006})\text{Ga}_2\text{O}_4)$ at 1,200 °C for 3 hours. As shown in this figure, the hyperfine structure of Mn^{2+} was not shown in raw powder mixture. However, in the sintered powder sample,

Fig. 6 Excitation spectra of $(\text{Zn}_{0.994}\text{Mn}_{0.006})\text{Ga}_2\text{O}_4$ and ZnGa_2O_4 monitored at 504 nm and 450 nm, respectively.

Fig. 7 ESR spectra of powder samples measured at room temperature:

a : raw powder mixture (ZnO , MnO , Ga_2O_3).
b : sintered powder sample $((\text{Zn}_{0.994}\text{Mn}_{0.006})\text{Ga}_2\text{O}_4)$.

ESR spectra appeared as six prominent lines with the resolved structure. All the lines are associated with the isolated Mn^{2+} ions¹²⁾, indicating the atomically homogeneous distribution of manganese. The hyperfine structure of Mn was very clearly shown in the sintered powder sample due to the substitution of Zn site of ZnGa_2O_4 by Mn ion. ESR data indicates that the Mn is incorporated in the ZnGa_2O_4 lattice on the Zn sites substitutionally. This leads to the hypothesis that the narrow bandwidth of green is due to Mn filling up Zn vacancies in the lattices. The incorporation of a small amount of Mn also leads to good crystallinity for the ZnGa_2O_4 host lattice as shown by X-ray diffraction data.

4. Concluding Remarks

The luminescence properties of the ZnGa_2O_4 phosphors prepared by solid state reaction method were studied with aids of mainly photoluminescence spectrometer, XRD, SEM, and ESR. The following conclusions of this work can be obtained:

- (1) All the phosphors prepared by solid state reaction method were well crystallized in the spinel-type structure.
- (2) The optimal reduction condition in 98 % N_2 -2 % H_2 atmosphere is thought to be a temperature of 900 °C.
- (3) The ZnGa_2O_4 phosphor exhibited a broad-band blue emission extending from 330 nm to 580 nm with peak at 450 nm.
- (4) The Mn^{2+} -doped ZnGa_2O_4 phosphor exhibited a

strong narrow-band green emission with peak 504 nm showed a maximum intensity at the Mn^{2+} concentration of 0.006 mol %. ESR analysis of the sintered powder sample revealed the substitution of Zn site of ZnGa_2O_4 by Mn ion.

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ZnGa_2O_4 蛍光体の合成およびその発光特性

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ZnGa_2O_4 蛍光体の発光特性およびその発光機構を調査する目的で、それを固相反応により合成した。試料粉末の生成相、発光特性、ドーピング特性を X 線回折法 (XRD)、発光-励起スペクトル (PL) の測定、電子スピン共鳴 (ESR) の測定などから実験的に検討した。254 nm 励起下で、 ZnGa_2O_4 蛍光体は 450 nm をピークにして、広いバンドの青色発光特性を示した。合成した蛍光体を弱に還元性雰囲気にして処理すると発光強度が大きく増

大した。また、 Mn^{2+} をドーピングした ZnGa_2O_4 蛍光体は 504 nm をピークにして、強く細いバンドの緑色発光特性を示した。そのとき、 Mn^{2+} のドーピング量を 0.006 % モルした ZnGa_2O_4 蛍光体が最大発光強度を示した。

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