Preparation and EPR Characteristics of ZnGa$_2$O$_4$: Mn Phosphor

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ZnGa$_2$O$_4$: Mn phosphors were prepared by a new chemical process, and their photoluminescence and electron paramagnetic resonance characteristics were investigated. The chemical method showed a low temperature formation of phosphors and a rod-type shape of particles. The strong ultraviolet emission was observed in the undoped ZnGa$_2$O$_4$ phosphor, while strong green emission in the Mn^{2+}-activated ZnGa$_2$O$_4$ phosphor. The green emission intensity of the phosphor prepared by the chemical method was much stronger than that prepared by the conventional method. This difference with preparation methods was interpreted as due to the difference in the distribution of Mn^{2+} in the host lattice. From EPR results, it was explained that the line intensity of the undoped ZnGa$_2$O$_4$ is associated with the electrical conductivity of this material and the concentration quenching of green luminescence of ZnGa$_2$O$_4$: Mn at higher Mn^{2+} concentration is attributed to the coupling by exchange interaction between Mn^{2+} ions.

Introduction

There is growing interest in ZnGa$_2$O$_4$ and Mn^{2+}-activated ZnGa$_2$O$_4$ as low-voltage operating phosphors for application in flat panel displays devices such as field emission displays (FED).[1,2] The zinc gallate phosphor was proven to have the excellent stability from results of high temperature operating lifetime measurement.[3] Also, its stability in high vacuum and the absence of corrosive gas emission under electron bombardment provide additional advantages over commonly used sulfide phosphors.[4] In addition, ZnGa$_2$O$_4$ exhibits blue emission without being doped with impurity, and also shows emission from green to red when it is doped with Mn^{2+} and Cr^{3+} ions.

The efficiency of phosphors has been increased by new synthesis technique and controlling the distribution of the activators in a host material. The luminescent properties of phosphors are strongly dependent on the particle size and crystal structure. Thus, the preparation conditions may be controlled to achieve better luminescent properties. Generally, zinc gallate phosphor is synthesized in powder by the solid-state reaction (conventional method) which employ high temperature firing, resulting in the agglomeration of phosphor particles. The subsequent crushing and ball milling processes damage phosphor surfaces resulting in the loss of the emission intensity.[5] For this reason, some recent investigations[6-8] have addressed development of alternative synthetic method. But only a few literatures[7-9] have been reported for preparing ZnGa$_2$O$_4$: Mn by wet chemical synthetic method. In addition, the formation of zinc gallate phosphor at low temperature is needed to reduce the loss of ZnO at high temperature due to its high vapor pressure. Phosphors for high efficiency require optimizing parameters such as particle size, shape of phosphors, and homogeneous distribution of activators in the host lattice.[10] We believe that this requirement can be met by a wet chemical synthetic method, which would yield uniform particle size with good crystallinity. We have prepared phosphors by wet chemical method and tried to improve their luminescent properties.

In the present work it was attempted to prepare ZnGa$_2$O$_4$:

Mn phosphors by the multi-stage precipitation method which is denoted as chemical synthetic method hereinafter and their luminescent properties were compared with those from the conventional method. The multi-stage precipitation method has been applied for preparation of ceramic powder in multi-components system.[11,12] Since it is difficult for Zn and Ga to co-precipitate in the solution without composition fluctuation, the multi-stage precipitation process, where Ga and Zn were precipitated by stepwise successively, has been designed. In addition, we have performed photoluminescence and EPR measurements to investigate the properties of ZnGa$_2$O$_4$: Mn phosphor prepared.

Experimental

Sample Preparation. Phosphors having the formula of Zn$_{1-x}$Mn$_x$Ga$_2$O$_4$ with x ranging from 0 to 0.03 were synthesized by the multi-stage precipitation method. The raw materials were high-purity Zn(NO$_3$)$_2$·6H$_2$O, Ga(NO$_3$)$_3$·xH$_2$O, and Mn(NO$_3$)$_2$·6H$_2$O (Aldrich) for the chemical method. Gallium nitrate was dissolved into distilled water, and then this gallium nitrate (1 M) solution was adjusted to pH 8 by 10%-NH$_4$OH. This suspension was heated up to at least 90 °C and kept at that temperature for 1 h. GaOOH seems to be precipitated in this step. The precipitate filtered was suspended into zinc nitrate (1 M) solution containing manganese nitrate. Then oxalic acid dissolved in ethanol was added in this suspension followed by an addition of diethylamine to adjust pH to 8.5. In this step, Zn (Mn) oxalate precipitate is formed. The resultant precipitate was filtered, allowed to dry, then fired in a reducing atmosphere of 5% H$_2$-95% N$_2$ with a flow rate of 10 mL/min, at 1100 °C for 4 h. Phosphors were also prepared by the conventional method. The starting materials were high-purity ZnO, Ga$_2$O$_3$, and MnCO$_3$ (Aldrich). Stoichiometric amounts of starting materials were thoroughly mixed in ethanol in a agate mortar and pestle, allowed to dry, then fired in a reducing atmosphere at 1100 °C for 4 h. On the other hand, ZnGa$_2$O$_4$ powder was pressed into 15 mm-diameter disks, then enclosed in the quartz ampoule. The disks were

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sintered at 1000 °C for 30 min in the hot isostatic pressing furnace. Apparent density of the sintered disks was about 60% of the theoretical density. A rectangular shaped sample cut from the sintered disk was used to measure the electrical conductivity.

Characterization. Crystalline phases and phase change of phosphors were checked by powder X-ray diffraction using a Rigaku DMAX-33 X-ray diffractometer with Cu-Kα radiation and by thermal analysis using a Dupont SDT-2960 TG-DTA analyzer at a heating rate of 5 °C/min. The morphology of the particles was observed by scanning electron micrograph using a Jeol JSM-840A SEM. Emission spectra were measured at room temperature with a Perkin-Elmer LS 50 luminescence spectrometer. Powder specimens were excited with 254 nm light source.[13] EPR measurements were recorded using an X-band Bruker ESP 300E spectrometer between 77 K and 500 K and referenced to DPPH as the g-value standard. The DC electrical conductivity of the ZnGa₂O₄ samples was measured using the standard four-point probe technique between room temperature and 500 K.

Results and Discussion

Preparation Characteristics. The thermal analysis results for the phosphor prepared by the chemical method, which were examined from room temperature to 1200 °C, are given in Figure 1. The DTA curve exhibits sharp endothermic peaks near 140 °C and 380 °C. The peak below 140 °C is originated from the evaporation of the water incorporated into the powder and the peak near 380 °C should be related to dissociation of oxalate groups, which induced the weight loss. The TG analysis for the phosphor formation reveals an onset of weight loss at *ca.* 100 °C, and completion of weight loss by 400 °C. No more significant weight loss is observed from 400 °C to 1200 °C. On the other hand, no appearance of a sharp exothermic peak is observed at higher than 400 °C. It indicates that the crystallization takes place slowly in this sample.
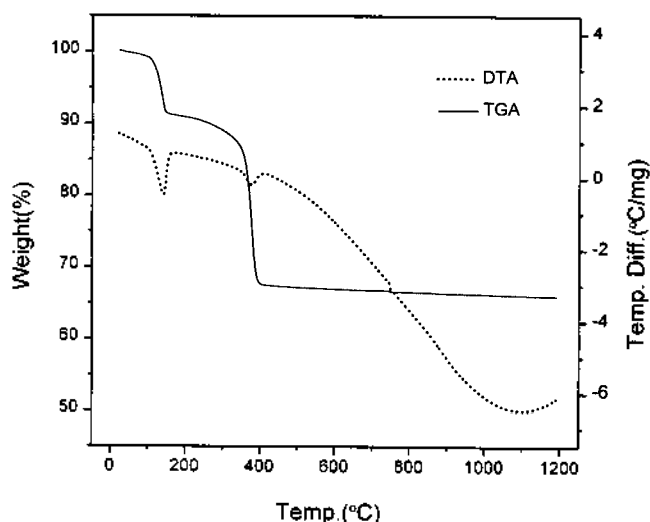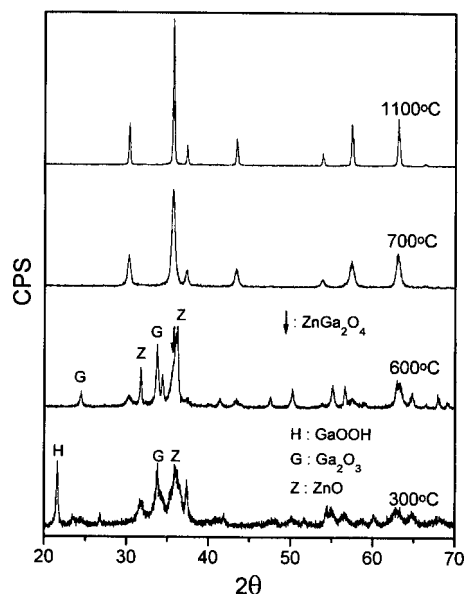
Figure 2 exhibits X-ray diffraction patterns of ZnGa₂O₄:

Figure 2. X-ray diffraction patterns of ZnGa₂O₄:Mn powders obtained by the chemical method at various temperatures.

Mn powders obtained by the chemical method fired at various temperature. In the diffraction pattern of the sample fired at 300 °C, the peaks due to GaOOH, ZnO, and Ga₂O₃ phases are observed. At 600 °C, the peaks of the Ga₂O₃, ZnO phases and also the main peak from (311) plane of ZnGa₂O₄ phase are clearly observed, so the formation of ZnGa₂O₄ starts from 600 °C. It is obvious that the single phase of zinc gallate was formed by firing at 700 °C. On the other hand, Shea *et al.*[13] reported that the crystallization of ZnGa₂O₄:Mn by the solid-state reaction is completed at 1100 °C. From the X-ray diffraction it can be noted that the formation temperature of ZnGa₂O₄:Mn phosphor by the chemical method which is attempted in this study is lower than that of the conventional method.

Scanning electron micrograph of phosphor obtained by the chemical method is shown in Figure 3. The particles of the phosphor appear rod-type and well-dispersed, whereas the phosphor particles by conventional method are shapeless and agglomerate as shown in a previous report.[9] This difference

Figure 1. TG-DTA curves for ZnGa₂O₄:Mn phosphor prepared by the chemical method.

Figure 3. SEM photograph of ZnGa₂O₄:Mn phosphor prepared by the chemical method.
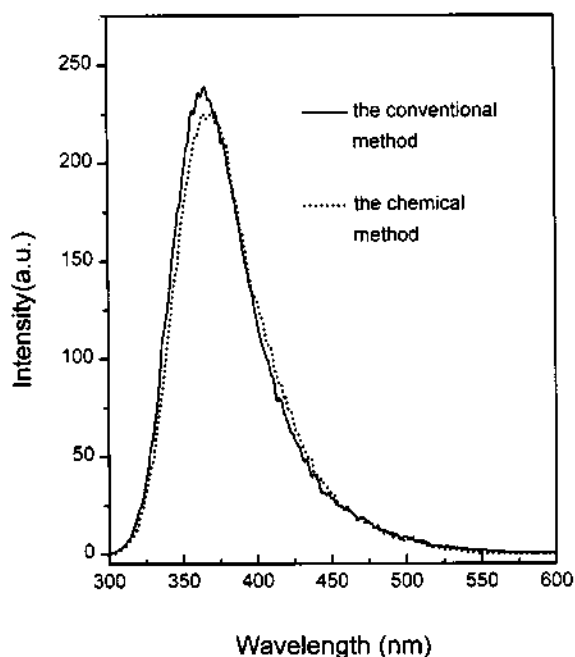
Figure 4. Emission spectra of the undoped $ZnGa_2O_4$ phosphors prepared by the conventional method and by the chemical method.

in the morphology could influence the luminescent properties of phosphor due to the damages and defects of phosphor surface.

Luminescence Characteristics. Figure 4 exhibits the emission spectra of the undoped $ZnGa_2O_4$ phosphors prepared *via* two processes. The broad emission bands centered near 370 nm are observed. There is no difference in the emission intensities. Poort *et al.*[14] reported the blue emission of $ZnGa_2O_4$ comes from gallate group. They added that a blue or ultraviolet gallate emission was also observed in other gallate compounds such as β-Ga_2O_3, $GaBO_3$. On the other hand, Yu and Lin[15] reported that the gallate emission was very sensitive to the ratio of ZnO and Ga_2O_3. They observed an emission shifting from the blue (460 nm) to the ultraviolet (350 nm) region as the mixing ratio changes from 1.3 : 1 to 1 : 1. Also, they suggested that their firing conditions caused a loss of ZnO which was high enough to reduce the $ZnO : Ga_2O_3$ ratio from 1.3 : 1 to around 1 : 1. This indicates that the $ZnGa_2O_4$ having a $ZnO : Ga_2O_3$ ratio of 1 : 1 after firing is shown the blue emission at 460 nm, whereas the Zn-deficient samples will be shown a shift to shorter wavelengths. Our emission spectra are in agreement with these results. It is observed that the emission bands of $ZnGa_2O_4$ have their maximums at ultraviolet regime. This observation can be suggested that our $ZnGa_2O_4$ samples are Zn-deficient, which explains the blue shift of the emission spectra in our samples compared to the 460 nm reported for the $ZnO : Ga_2O_3$ ratio of 1 : 1. The powder density (about 5.6) of $ZnGa_2O_4$ samples was lower than its theoretical value (6.15). This fact supports that a loss of ZnO in our samples took place.

Figure 5 compares the emission spectra of $Zn_{1-x}Mn_xGa_2O_4$ (x=0.005) phosphors prepared according to the two processes. Although both samples showed the green emission at 505 nm, the emission intensity of the phosphor obtained by the
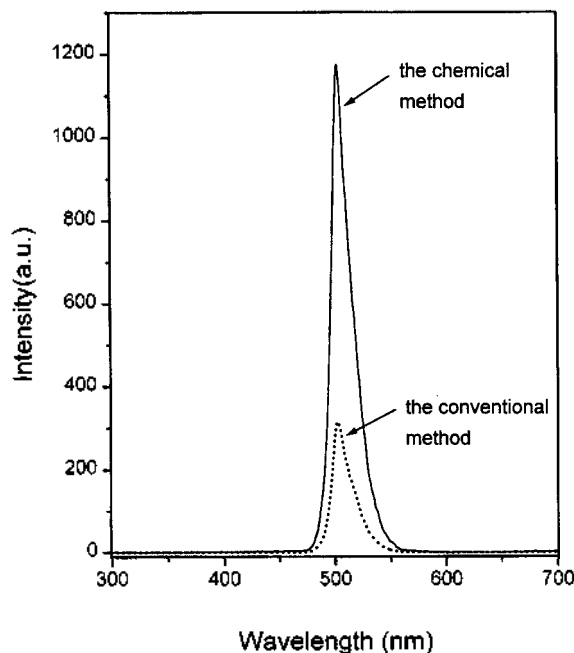

Figure 5. Emission spectra of $Zn_{1-x}Mn_xGa_2O_4$ (x=0.005) phosphors obtained by the conventional method (dotted line) and by the chemical method (solid line).

chemical method is at least three times as strong as that by the conventional method. $ZnGa_2O_4$ is known to have a normal spinel structure with Zn^{2+} ions in tetrahedral sites and Ga^{3+} ions in octahedral sites. For the Mn^{2+}-activated $ZnGa_2O_4$ phosphor it was reported that green emission is assigned to the transition $^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} ion in a four-coordinated environment.[14-16] This is in good agreement with the result of the emission at 505 nm from $ZnGa_2O_4 : Mn$ in this study.
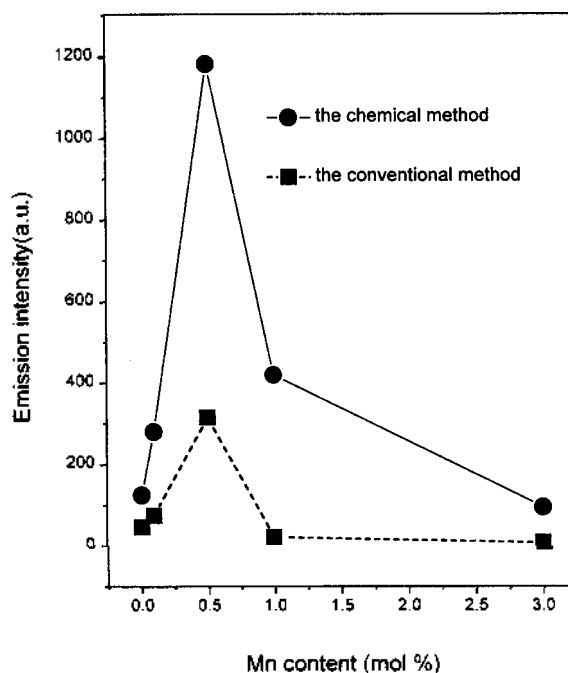

Figure 6. The relationship between green emission intensities and Mn contents in Mn^{2+}-activated $ZnGa_2O_4$ phosphors.

In Figure 6, the emission intensities with Mn contents in the ZnGa₂O₄ : Mn phosphors are given. The emission intensity increases with the concentration of Mn in the host material at lower Mn content region. It reaches maximum at Mn concentration of 0.5 mol %, and then decreases with increasing Mn content indicating concentration quenching. Both the emission intensities of the Mn²⁺-activated ZnGa₂O₄ phosphors prepared by the chemical method are higher than those prepared by the conventional method. This difference in the emission intensities of the ZnGa₂O₄ : Mn phosphors with the preparation methods may be regarded as due to the difference of homogeneity in the distribution of Mn ions in the host lattice.

EPR Study. The EPR spectrum of the undoped ZnGa₂O₄ powder measured at room temperature are given in Figure 7(a). In addition, EPR spectra of ZnO and Ga₂O₃ are compared to that of ZnGa₂O₄ sample. ZnO and Ga₂O₃ were each fired separately on the same firing conditions as ZnGa₂O₄ phosphor. Although the g values of both EPR signals are the same as 1.96, the EPR spectrum pattern of ZnGa₂O₄ is more similar to that of Ga₂O₃ compared with ZnO. Since these compounds have no paramagnetic ions, these EPR signals can be due to the point defects in the crystals. The EPR signal g=1.96 of ZnO sample, according to Koudelka,[17] can be ascribed to the singly ionized oxygen vacancy $(V_O{}^{\cdot})$. Vanheusden *et al.*[18] reported that oxygen vacancy in pure ZnO phosphors was found to play an important role in their green luminescence. They explained that the green emission intensity in ZnO phosphor is proportional to the number of paramagnetic $V_O{}^{\cdot}$ center, which indicates that the singly ionized oxygen vacancy is responsible for the green emission. However, the situation seems to be different in case of ZnGa₂O₄ phosphor. The blue emission of ZnGa₂O₄ phosphor is quenched, while its EPR line intensity increases with the increase of temperature. On the other hand, Aubay
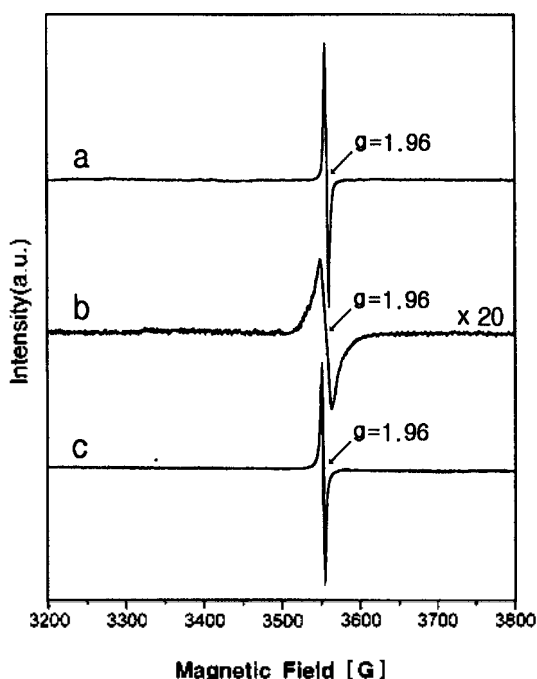
and Gourier[19] conjectured that the EPR signal g=1.96 of β-Ga₂O₃ sample was due to conduction electrons. This compound is normally an insulator, but it becomes an n-type semiconductor $(\sigma=10^{-1}\ \text{S·cm}^{-1})$ when it is fired under reducing conditions. The donor levels probably originate from oxygen vacancies. Upon excitation with 254 nm, the reduced β-Ga₂O₃ exhibits a blue emission at 413 nm.[14] Therefore we assume that the luminescence properties and EPR spectrum of the undoped ZnGa₂O₄ phosphor are similar to those of the β-Ga₂O₃.

The dependence of the electrical conductivity and EPR line intensity of ZnGa₂O₄ with temperature is given in Figure 8. It is noted that these two values varied in quite a similar pattern with temperature. In general, conduction electrons in n-type oxide semiconductors are generated from interstitial or oxygen vacancies or substituted cations. Omata *et al.*[20] reported that the conductivity $(\sigma=30\ \text{S·cm}^{-1})$ of ZnGa₂O₄ increase drastically on going from oxidizing to reducing conditions. This indicates that the formation of conduction electrons is enhanced under reducing conditions and the conduction electrons are originated from oxygen vacancies. The electrons might be excited thermally from the oxygen vacancies to the conduction band of ZnGa₂O₄. In Figure 8, it is observed that the electrical conductivity of ZnGa₂O₄ sample exhibits strong temperature dependence. This means that the increase in conductivity with raising temperature is caused by the increase in the concentration of the conduction electrons. Thus, it is to be concluded that the EPR signal from ZnGa₂O₄ sample is attributed to the conduction electrons and the undoped ZnGa₂O₄ is an n-type semiconductor. In addition, the conductivity measured for ZnGa₂O₄ sample by Omata *et al.* is higher than that by this study. The color of their sample was light blue, while the color of our sample white. This discrepancy can presumably be considered as due to the difference in firing conditions. Their sample was sintered at 1300 °C for 48 h and annealed in reducing atmosphere of H₂ gas only, which could
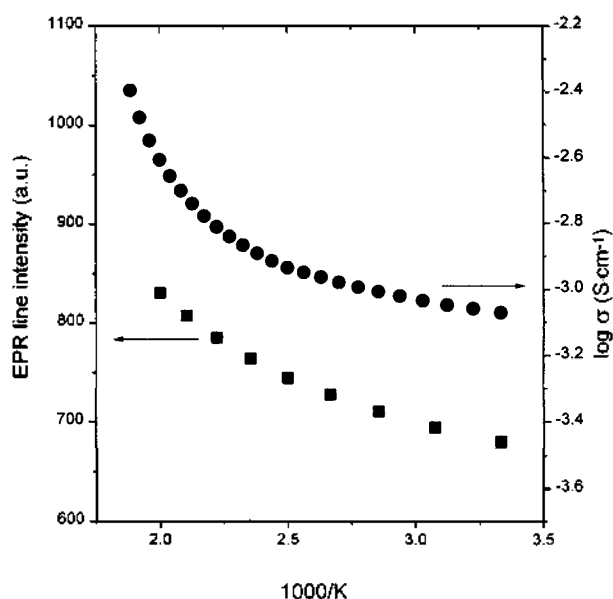

Figure 7. EPR spectra of ZnGa₂O₄ (a), ZnO (b), and Ga₂O₃ (c) powders measured at room temperature.

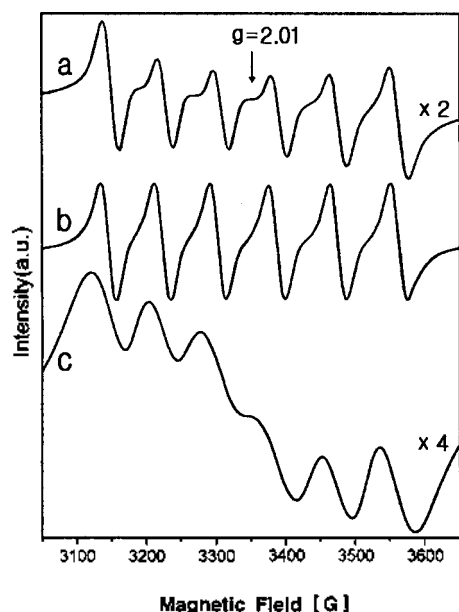**Figure 8.** Dependence of the electrical conductivity and EPR line intensity of ZnGa₂O₄ on temperature.

Figure 9. EPR spectra of $Zn_{1-x}Mn_xGa_2O_4$ powders with $x=0.005$ by the conventional method (a) and by the chemical method (b), and with $x=0.03$ by the chemical method (c).

Figure 10. Dependence of EPR line intensity on Mn concentration of $ZnGa_2O_4$:Mn prepared by the chemical method.

generate higher apparent density of the sintered body and higher concentration of the conduction electrons that are formed by oxygen vacancies. For application in the low-voltage cathodoluminescence devices such as the field emission displays, the conductance of phosphor is required to prevent the charge accumulation by electrons on phosphor surface, which result in high efficiency of phosphor.

Figure 9 shows EPR spectra of $Zn_{1-x}Mn_xGa_2O_4$ powders prepared by two methods. The g value of the EPR spectra due to Mn^{2+} is calculated to 2.01. EPR spectra of manganese in the zinc gallate spinel phase correspond to hyperfine transitions with $\Delta M_I=0$ and the fine structure transition with $\Delta M_S=\pm1$, $M_S=1/2$ to $M_S=-1/2$. Since the luminescent center in $ZnGa_2O_4$:Mn phosphor is obviously manganese ions, a homogeneous distribution of Mn^{2+} ions in host material is required. In EPR spectrum of the $Zn_{1-x}Mn_xGa_2O_4$ ($x=0.005$) powder prepared by the chemical method, six hyperfine lines with high resolution are observed (see Figure 9(b)). These might be associated with a homogeneous distribution of manganese. However, when the Mn^{2+}-activated $ZnGa_2O_4$ phosphor was prepared by the conventional method, there is a difference in the relative intensity of six hyperfine lines as shown Figure 9(a). This would be caused by an inhomogeneous distribution of manganese in the host crystal.[21,22] From the EPR results given and discussed above, the difference in the emission intensities of $ZnGa_2O_4$:Mn phosphors prepared by the chemical method and the conventional method is attributed to the difference in the distribution of Mn^{2+} ions in the host lattice. And also the EPR signal intensity of the phosphor by the chemical method is higher than that by the conventional method. This can be explained by the higher number of isolated Mn^{2+} ions of the sample obtained by the chemical process due to a homogeneous distribution of manganese.

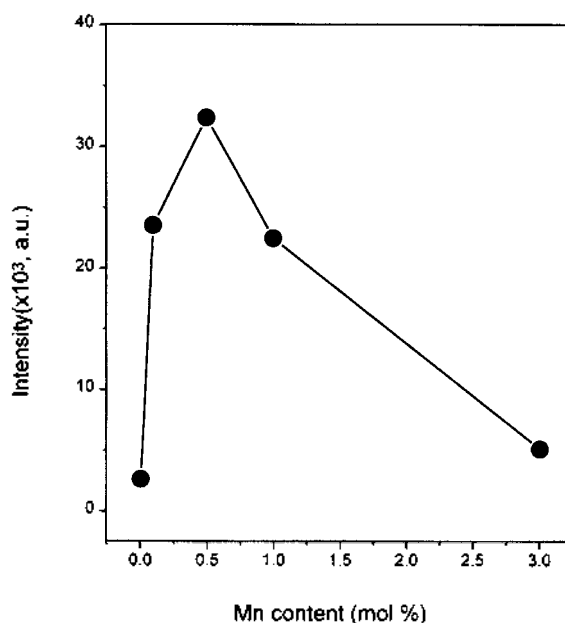On the other hand, EPR spectra at lower Mn content in $ZnGa_2O_4$:Mn exhibited the resolved structure with six

prominent lines. With increasing interaction between Mn^{2+} ions the six hyperfine lines became broader and unresolved with different intensities, and finally merged into a structureless single line. When Mn^{2+} ion concentration grew greater than 0.5 mol %, there was the appearance of EPR line broadening. At Mn^{2+} concentration of 3 mol %, the EPR spectrum appeared as six broad lines with an unresolved structure, as seen Figure 9(c). This can be interpreted by the formation of Mn^{2+} pairs or clusters, since the EPR line broadening is mainly caused by Mn^{2+} ions coupled by exchange interaction.[23] The dependence of EPR line intensity on Mn^{2+} concentration of $ZnGa_2O_4$:Mn phosphors prepared by the chemical process is shown in Figure 10. As can be seen, EPR line intensities with Mn^{2+} concentration change such a manner as the emission intensities with Mn^{2+} concentration (see Figure 6). It is confirmed that the decrease of the EPR line intensity and the concentration quenching of the green luminescence occur in the vicinity of 0.5 mol % Mn^{2+}. The concentration quenching of luminescence can be explained by electron and energy transfers between Mn^{2+} ions coupled by exchange interaction. The probability of nonradiative transition by these transfers may be increased at higher Mn^{2+} concentration due to spin-spin and spin-lattice exchange interaction. Thus, it is to be concluded that the concentration quenching of luminescence in the Mn^{2+}-activated $ZnGa_2O_4$ phosphors is attributed to the formation of Mn^{2+} ion pairs or clusters caused by an inhomogeneous distribution of manganese.[22]

Conclusions

In this work, $ZnGa_2O_4$:Mn phosphor preparation was designed by the multi-stage precipitation method to improve the luminescent properties. We have demonstrated that this chemical synthetic method is a useful process to obtain the uniform phosphor with well-dispersed particles for $ZnGa_2O_4$: Mn system. The following conclusions were obtained from

this study. The designed method featured a low temperature formation of phosphors and their rod-type shape in the morphology. The green luminescent properties of the Mn^{2+}-activated $ZnGa_2O_4$ phosphors prepared by this method were much stronger than those prepared by the conventional method. At Mn^{2+} concentration of 0.5 mol %, the 505 nm emission intensity of the phosphor obtained by the chemical method was three times as strong as that by the conventional method. From the EPR measurements, it was found that the EPR line intensity of the pure $ZnGa_2O_4$ is associated with the electrical conductivity of this material. The improvement in the emission intensity of the Mn^{2+}-activated $ZnGa_2O_4$ phosphor by the chemical method was attributed to a homogeneous distribution of Mn^{2+} ions in the host lattice. Also, it is confirmed that the luminescence concentration quenching in the Mn^{2+}-activated $ZnGa_2O_4$ phosphors was caused by the formation of Mn^{2+} ion pairs or clusters.

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