

Photoluminescence of the Mn-doped ZnGa₂O₄ Phosphors Prepared by Coprecipitation of Metal Salts

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Manganese-activated zincgallate (Zn_{1-x}Mn_xGa₂O₄) phosphor as a green phosphor was readily prepared by coprecipitation in aqueous basic solution of metal salts. The obtained product converted to amorphous zincgallate even at 300 °C, followed by crystallization at 1000 °C. The pyrolyzed phosphor showed fine particle, then reduction treatment at 900 °C changed into homogeneous shape with slight grain growth (particle size less than 0.5 μm). The photoluminescence characteristics of the zincgallates have been investigated as a function of dopant concentrations, reducing atmospheres and temperatures. Under UV excitation the phosphors displayed the highest green emission efficiency at 504 nm when the specimen oxidized at 1000 °C was reduced at 900 °C in a mild hydrogen atmosphere (97% N₂, 3% H₂) with a flow rate of 100 ml/min.

Introduction

Various emissive phosphors are used in most display technologies, including electroluminescent, cathode ray tube, field emission, plasma and liquid crystal, as direct light emitters or as illumination sources. The performance of display products depends upon phosphor efficiencies, spectral distribution, long-term stability and electrical characteristics. Often there are constraints of emissive materials that limit improvements in displays.¹ Particularly, the phosphors for plasma displays need a breakthrough in luminous efficiency, greater long-term stability in a gas plasma, and better thick-film deposition processes.²

Zincgallate itself shows blue emission with relatively low efficiency while manganese-activated zincgallate is an efficient green emitting phosphor for field emission display (FED) which is emerging as a potential substitute to the present liquid crystal display (LCD) technologies with low profitability.³ It is known that stability of the phosphors in high vacuum and the absence of corrosive gas emission under electron bombardment offers advantages over sulfide phosphors commonly used for vacuum fluorescent display.^{1,3,4}

Much work has been concerned physical mechanism of the luminescence and phosphorescence in zincgallate phosphors. In the literatures, green emission results from the substitution of Zn⁺² ions with Mn⁺² ones in spinel structure of zincgallate. Zn_{1-x}Mn_xGa₂O₄ both as an activator and host-to-activator sensitized phosphor absorbs energy from electron beams,⁵ followed by energy transfer to Mn⁺² emission center to emit light. In addition, it has been known that the essential requirements for low-voltage cathodoluminescent phosphors are low resistance and low threshold voltage as well as excellent crystallinity.^{4,6}

Zincgallate powder has been prepared from zinc oxide and gallium oxide by conventional solid state reaction, sintering at 1200 °C for highly extended heating times.^{4,6} In this context, sol-gel process is an attractive synthetic route for prepa-

ration of multicomponent ceramic oxides, since a homogeneous mixture of the several component at a molecular level can be easily reached in solution. In addition to greater homogeneity and purity of the product, the sol-gel method allows a low processing temperature and morphological control of a uniform crystalline-particle size at superfine dimension. To the best of our knowledge, there has been surprisingly no work on the simple sol-gel techniques to synthesize the zincgallate phosphor with high homogeneity and crystallinity at low temperatures.

In the present work, we report the successful synthetic route of zincgallate by coprecipitation in aqueous basic solution of metal salts, and its pyrolytic conversion to inorganic oxide. And the photoluminescence of the phosphor prepared at various conditions is also evaluated to optimize its emission performance.

Experimental Section

Synthesis. Phosphors with the general formula Zn_{1-x}Ga₂O₄ : Mn_x have been prepared by using the precipitation method as shown in Figure 1.

The raw materials (1-x) mol% Zn(NO₃)₂·H₂O (Aldrich, 99.999%), 2 mol% Ga(NO₃)₃·H₂O (Aldrich, 99.9%) and x mol% Mn(CH₃COO)₂ (Aldrich, 98%) as a dopant were dissolved stoichiometrically by stirring in distilled water or ethanol-water mixture (90 : 10 vol.%) at room temperature. Then ammonium hydroxide was added into the solution for precipitation until the solution finally reached a pH value of 7-7.5.

After aged for hours, this suspension was heated in a rotary vacuum evaporator to remove solvent at 50 °C, followed by drying at 80 °C. The slurry product displayed white color while the slurry obtained under pH ~9 showed pink color. The slurry product was completely dried when heated to 300 °C using a heating mantle. The prepared raw phosphor powder was finely ground for calcination at 500 °C-1000 °C for 3 hours in a muffle furnace under air atmo-

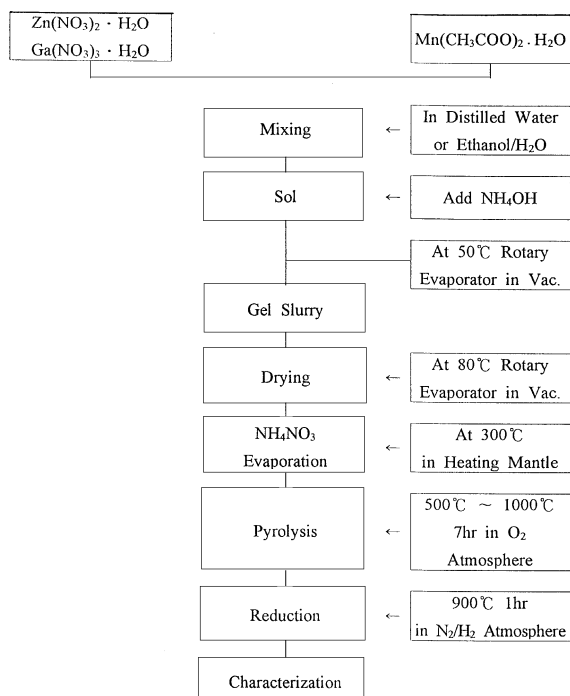


Figure 1. Overall synthetic route for preparation of $Zn_{1-x}Mn_xGa_2O_4$ phosphor.

sphere. The reduction of the calcined phosphor was performed using a tube furnace in a mild reduction atmosphere containing 97% N_2 and 3% $H_2(N_2/H_2)$. The samples were heated for a period of one hour at 800 °C-1000 °C with various flow rate. The flow rate was controlled by LINDE (UCC P/N FM 4332 unit milliliter/min) gas flow meter.

Characterization. The phosphors were characterized by x-ray diffraction analysis using a Rigaku Model DMAX-33 X-ray diffractometer with $Cu-K\alpha$ radiation operating at 35 kV, 15 mA, and 4° of $2\theta/\text{min}$ scanning rate. The morphology of the phosphor was observed by scanning electron microscopy (SEM). Thermal decomposition and phase transformation of the initial product were monitored with a SHIMADZU DTA 50 and TA instruments TGA 2050 Thermal analyzer in dry air at a heating rate of 10 °C/min. The photoluminescence (PL) measurements of the prepared phosphors were conducted by using a spectrometer (Spex. 1404P) photoluminescence measurement system. Samples were packed in a NMR tube (Aldrich) and excited with 325 nm laser radiation⁷ from HeCd laser (Omnichrome 41, 40 mW). The emission wavelength was monitored from 350 nm to 650 nm (Slitwidth = 2 mm, Integration time = 1 msec.) using CCD array detector (Spex Spectrum One, 1800 gr/mm resolution) at room temperature.

Results and Discussion

Synthesis. Overall reaction of metal salts could be summarized as the following equation;



It is known that zinc nitrate is readily hydrolyzed to $Zn(OH)_2$ while gallium nitrate mainly converts to its hydrous oxide, $GaOOH$, in aqueous basic solution. And also conversion between $GaOOH$ and $Ga(OH)_3$ is similar to the aluminum analogues of boehmite ($AlOOH$) and bayerite ($Al(OH)_3$).⁸

During the hydrolysis of two nitrates, subsequent condensation between two metal hydroxides may lead to coprecipitated products with hydrox (-OH-) or oxo (-O-) bridges.⁹ However, when the precipitated product was washed with distilled water to eliminate ammonium nitrate, it always produced the zincgallate containing excess ZnO which is known to give low luminescent property.¹⁰ It may indicate that gallium oxide derivatives are more soluble in water due to slow reaction kinetics compared to zinc derivatives. Thus, the solvent drying process was applied for obtaining stoichiometric products without loss of less reactive species. Alternatively the ammonium nitrate could be washed off from the stabilized product treated above at least 200 °C.

Thermal properties of the slurry product was determined by using DTA/TGA as shown in Figure 2. It is appeared that the broad endothermic peak at 100 °C is attributed to the dehydration of the slurry. The pronounced endothermic peak near 150 °C is attributed primarily to evaporation of ammonium nitrate as a byproduct, corresponding to weight loss of 5% in TGA curve. The presence of ammonium nitrate was also confirmed by X-ray diffraction of the powder sublimed on heating the slurry to 300 °C. It is believed that the sharp exotherm at 300 °C indicates the pyrolytic condensation of residual metal salts or hydroxides in air, involving a weight loss of 10%. The broad exotherm in the temperature range 500-900 °C is related with crystallization of zincgallate without further weight loss.

The structural evolution of zincgallate treated at various

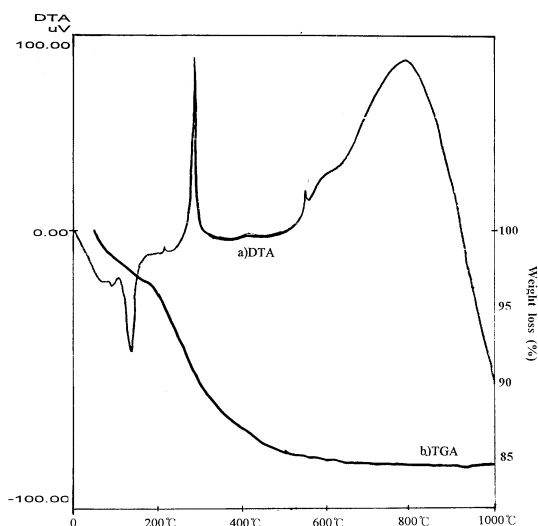


Figure 2. Thermal properties of the precipitated slurry product. a) DTA, b) TGA.

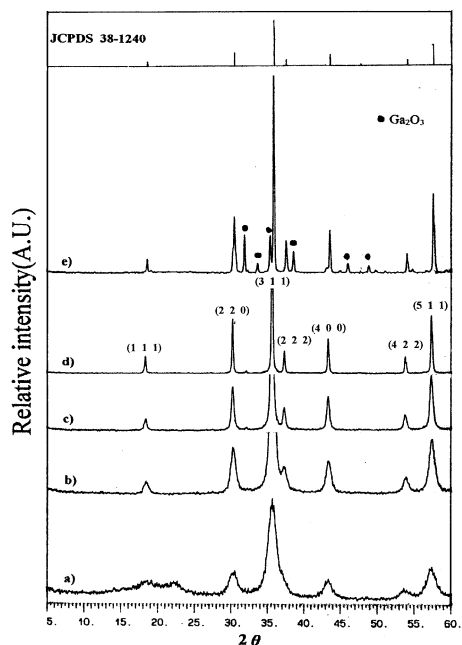


Figure 3. Powder X-ray diffraction patterns of Zn_{1-x}Mn_xGa₂O₄ treated at a) 300 °C, b) 500 °C, c) 800 °C for 7 hours in air, e) followed by reduction at 900 °C for 1 hour.

temperatures was determined by powder x-ray diffraction patterns as shown in Figure 3. Interestingly, the specimen annealed only at 300 °C already displays the diffuse diffraction corresponding to amorphous zincgallate. As the structure is heated to higher temperatures of 500 °C, crystalline phase begins to develop the diffraction pattern with narrower width, indicating grain growth. Extended heating at 1000 °C for 7 hr produced a pure single spinel phase of zincgallate. On the other hand, reduction treatment of the phosphor at 1000 °C results in the formation of zincgallate including excess Ga₂O₃ due to evaporative loss of ZnO at the high temperature, as reported by other work.^{11,12} It was observed even at 900 °C with less extent of crystalline Ga₂O₃.

The morphology of phosphor powder was observed by SEM photograph in Figure 4. The product pyrolyzed at 1000 °C shows finely agglomerated particles. And the phosphor reduced by H₂ gas at 900 °C changes into homogeneous shape of larger particles with slight grain growth (less than 0.5 μm in diameter), but reduction at 1000 °C leads to sintering of powder.

PL Measurement. Zincgallate (ZnGa₂O₄) is well-known as a blue emission phosphor which has a spinel structure with all of Zn⁺² ions in tetrahedral (*T_d*) sites and Ga⁺³ ions in octahedral (*O_h*) sites.¹³ It is well known that it converts to a green emission phosphor by the introduction of manganese dopant.⁴⁻⁶ The substitution of Zn⁺² (*r*_{Zn⁺²} = 0.74 Å) by Mn⁺² (*r*_{Mn⁺²} = 0.80 Å) shifts the emitted light to yellow due to distorted *T_d* sites.¹³ It has been reported that the ZnGa₂O₄ doped by 0.005 mol% or 0.006 mol% Mn showed excellent green emission properties.^{3,4}

Thus, we determined the luminescence properties of the phosphors doped with the same concentrations of Mn

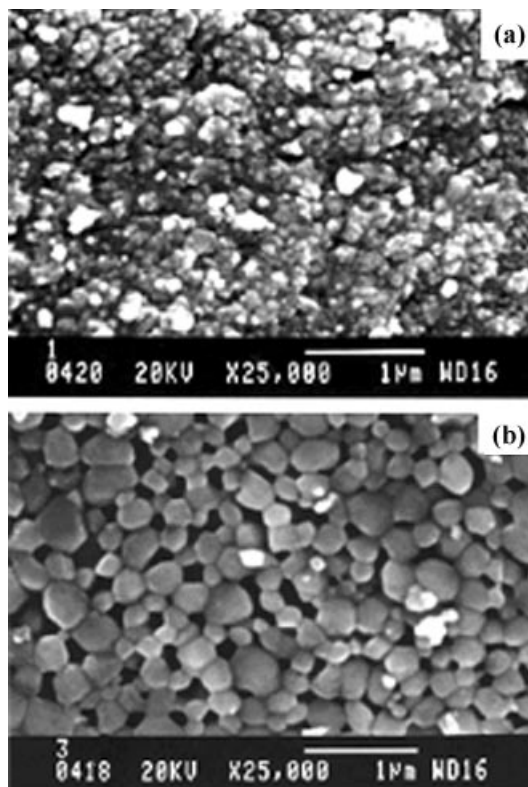


Figure 4. SEM morphology of Zn_{1-x}Mn_xGa₂O₄ powders a) pyrolyzed at 1000 °C in air, and b) reduced at 900 °C in a N₂/H₂ atmosphere.

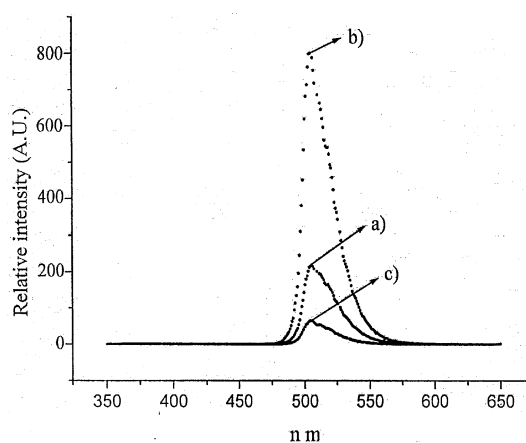


Figure 5. Photoluminescence spectra of Zn_{1-x}Mn_xGa₂O₄ (*x*=0.005 mole%) treated at 1000 °C in air and subsequently reduced at a) 800 °C, b) 900 °C, c) 1000 °C under N₂/H₂ gas with a flow rate of 100 ml/min.

dopant. Figure 5 shows the emission spectra of Zn_{1-x}Mn_xGa₂O₄ (*x* = 0.005 mol%) phosphors which was treated at 1000 °C in air and subsequently reduced at various temperatures in a N₂/H₂ gas flow rate of 100 ml/min. The prepared specimens of Zn_{1-x}Mn_xGa₂O₄ exhibit green emission at 504 nm which is consistent with previous reports.^{3,4} The phosphor reduced at 900 °C displays the strongest green emission intensity while the ones reduced at 800 °C and 1000 °C show relatively weak emission spectra. It may imply that most

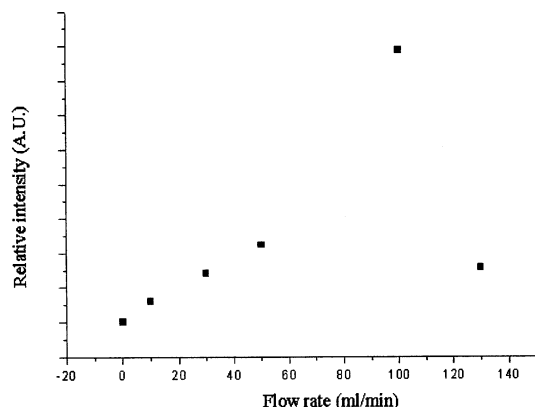


Figure 6. Emission intensity of $Zn_{1-x}Mn_xGa_2O_4$ ($x=0.006$ mole%) as a function of N_2/H_2 flow rate when reduced at $900^\circ C$ for 1 hour.

highly oxidized manganese (III, IV) species formed during oxidative pyrolysis¹⁴ could not be reduced at $800^\circ C$ to Mn^{+2} in the four-coordinated position of the spinel structure.^{3,4} However, inhomogeneous grain growth at $1000^\circ C$ led to weak green emission. In this point, it is noteworthy that homogeneity of fine particle phosphor is required for high emission.³ On the other hand, unsymmetrical shape of emission spectra was observed presumably due to excess Ga^{+3} ions which cause a high vacancy concentration. The vacancy defects would perturb randomly the atomic configuration and the associated crystal field surrounding the Mn^{+2} ions. Consequently, the ground level and excited level of the optically active electrons in Mn^{+2} ions tend to spread, leading to shape of the obtained spectra.

When the phosphors pyrolyzed at $1000^\circ C$ were reduced at $900^\circ C$ for 1 hour under various flow rates of the mixed N_2/H_2 gas, Figure 6 shows effect of the flow rates on the emission behavior of $Zn_{1-x}Mn_xGa_2O_4$ ($x: 0.006$ mole%). It was confirmatively observed that the un-reduced phosphor showed only tiny green emission intensity at 504 nm. And second firing in mild hydrogen atmosphere changed from peach body color to white. The emission intensity of the phosphor generally tends to increase as the flow rate increases. That is, the specimen reduced at a flow rate of 100 ml/min shows outstanding emission intensity while the ones reduced at 130 ml/min obviously decreases emission intensity. The former condition may fully activate luminescent property by reduction of the highly oxidized Mn species. However the latter condition lead to excessive evaporation of ZnO, resulting in highly excessive Ga_2O_3 phase. In addition, the raw phosphor precipitated at pH 9 solution showed pink body color,¹⁵ the emission was very weak even after reduction in N_2/H_2 atmosphere.

In Figure 7 shows emission properties of phosphors prepared by hydrolysis in distilled water or ethanol-water (90 : 10 vol.%) solution. The samples were treated at optimum conditions; oxidation at $1000^\circ C$ followed by reduction at $900^\circ C$ in a flow rate of 100 ml/min. Both spectra exhibit great green emission without distinct difference although the precipitate obtained from distilled water produced slightly more uniform particles than the powder from ethanol-water

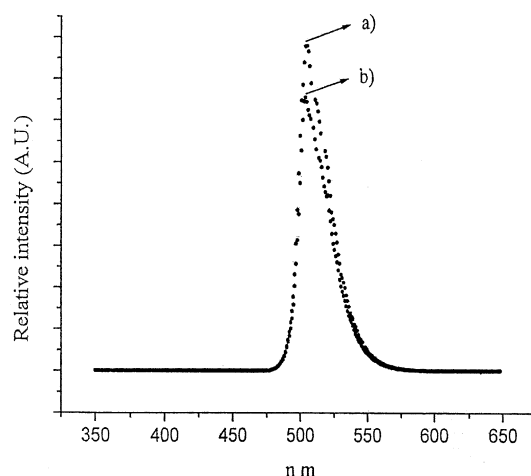


Figure 7. Emission spectra of $Zn_{1-x}Mn_xGa_2O_4$ ($x=0.006$ mole%) prepared by hydrolysis in a) distilled water or b) ethanol-water (90 : 10 vol.%) solution.

solution. It means that the conditions for post-treatments have dominant influences on photoluminescence of the phosphors prepared by the coprecipitation method.

Conclusions

The pure $Zn_{1-x}Mn_xGa_2O_4$ as a green phosphor was readily prepared by the coprecipitation of two nitrate in aqueous basic solution. Furthermore, the homeogenous precipitate was pyrolyzed to form well-crystalline phosphor at comparatively low temperatures ($<1000^\circ C$) while the conventional method from Ga_2O_3 and ZnO powders is required to anneal at $1200^\circ C$. And when the oxidized samples at $1000^\circ C$ were reduced by the mixed N_2/H_2 atmosphere at $900^\circ C$ in a flow rate of 100 ml/min, the phosphors show the highest emission efficiency at 504 nm. Particularly, this work proved that the newly developed method could replace the conventional method with considerable reliability on luminescent properties.

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