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Characteristics of nano-sized $ZnGa_2O_4$ phosphor prepared by solution combustion method and solid state reaction method

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Abstract

$ZnGa_2O_4$ phosphors were prepared by both SCM (solution combustion method) and SSRM (solid state reaction method). The properties of the both $ZnGa_2O_4$ phosphors were investigated by TGA (Thermogravimetric analysis), SEM (scanning electron microscope), BET (Brunauer Emmett Teller), PL (photoluminescence) and XRD (X-ray diffraction). The particle size of SCM phosphor was about one-hundredth of SSRM phosphor. The PL intensity of SCM phosphor was about 1.5-fold higher than that of SSRM phosphor. The SCM phosphor was also tried to be doped with Mn^{2+} ions. The highest PL peak was observed with Mn^{2+} ions of 0.003 mol fraction. The peak was shifted from blue (470 nm) to green (513 nm) color. These results might be very useful for high efficiency phosphors for displays such as field emission displays and plasma display panels.

Keywords: Solution combustion method; Powders-solid state reaction; ZnO; Impurities; Optical properties

1. Introduction

FEDs (field emission displays) have recently gained much attention as they are considered next generation flat panel displays. Especially of great interest are SEDs (surface-conduction electron-emitter displays) which are the type of FED, because of their relative ease of fabrication (no emitter tips) and low energy consumption. The energy consumption of SEDs is even lower than that of CRTs. Their energy consumption depends very much on the emission efficiency of phosphors. The high efficiency phosphors are therefore one of key technologies for the SEDs. Sulfide type phosphors are presently commercially available. However, they were developed for CRTs. These phosphors could generate sulfide gas and result in corrosion of emission tips (FEDs) or electron emitting electrodes (SEDs) since they are operated under high vacuum condition. Furthermore, low power consumption is essential for portable displays. These requirements make many researchers work on oxide type phosphors such as $ZnGa_2O_4$ phosphors.[1–8]

Recently, this research group proposed the solution combustion method to synthesize highly pure nano-sized metal oxide powders. Using this method, the heating and evaporation of metal nitrate solution with glycine result in self-firing and generates intense heat by exothermic reaction. Due to its high temperature and pressure reaction condition, highly pure nano-sized metal oxide powders could be synthesized.[9] In this paper, undoped and Mn-doped $ZnGa_2O_4$ phosphors were prepared by both SCM and SSRM. The properties of these $ZnGa_2O_4$ phosphors will be discussed with comparison.

2. Experimental

$Zn(NO_3)_2{\cdot}6H_2O$ (Junsei Co.) and $Ga(NO_3)_3{\cdot}6H_2O$ (Aldrich Co.) powders were used for starting materials to prepare SCM $ZnGa_2O_4$ powders. The starting materials were dissolved in distilled water in beaker. Glycine (Yakuri pure chemicals Co. Ltd) was then added to the starting solution as a fuel. Here both Zn and Ga nitrates act as oxidants during reaction. The mixture solution in the beaker was heated on hot plate with stirring. As the distilled water was evaporated, the mixture solution was heated to be exploded and eventually combusted. Here the heating temperature was only 100 °C to evaporate water. The nitrate ions (NO_3^-) reacted with the fuel and intense heat was generated (about 1500–1800 °C). This high temperature resulted in high pressure. This instantaneous high pressure led to explosion. The

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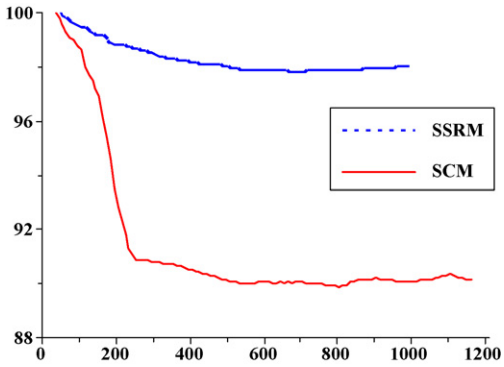

Fig. 1. TGA graphs of $ZnGa_2O_4$ powder (a) prepared by SSRM and (b) prepared by SCM.

$ZnGa_2O_4$ powders were formed in this high temperature and pressure environment. At this point the powders were gathered up by the collector, which was placed above the beaker. Here all the experiment was performed inside stainless steel chamber for safety. The SCM $ZnGa_2O_4$ powders were calcined at 400 °C for 1 h to remove organic remains. To dope the SCM $ZnGa_2O_4$ powders with Mn, $Mn(NO_3)_2{\cdot}xH_2O$(Aldrich Co.) powders were mixed with starting materials. Then it was followed by same procedure mentioned above.

On the other hand, ZnO (Junsei Co.) and Ga_2O_3 (Aldrich Co.) powders were used for starting materials to prepare SSRM $ZnGa_2O_4$ powders. They were mixed with ethanol and ball-milled for 24 h. Then they were dried at 400 °C for 30 min. To obtain SSRM $ZnGa_2O_4$ powders, the mixed powders were calcined at 1200 °C for 10 h. The properties of the both $ZnGa_2O_4$ phosphors were investigated by TGA, SEM, BET, PL and XRD.

3. Results and discussion

As shown in Fig. 1(a), the weight of reacting powders decreased when they were calcined up to 600 °C. At lower temperature region, it decreased rapidly because the ethanol used during ball-milling was removed. At higher temperature region, the reaction between ZnO and Ga_2O_3 powders would be started. At higher than 600 °C, $ZnGa_2O_4$ powders would be formed. Uheda et al. reported that the solid state reaction is completed above 1000 °C.[10] The SCM $ZnGa_2O_4$ powders were also tried to calcine up to 1200 °C to see if there is any weight change. Fig. 1(b) shows that the organic remains were removed at near 200 °C. There was almost no weight change after 200 °C.

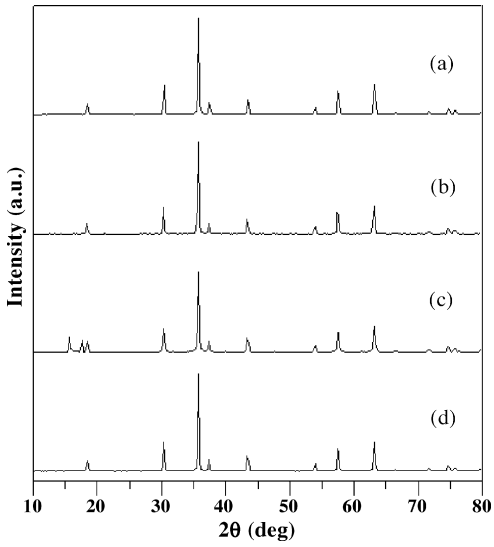

Fig. 2. XRD patterns of $ZnGa_2O_4$ powder (a) calculated, (b) prepared by SSRM (1200 °C, 10 h), (c) prepared by SCM (as synthesized) and (d) prepared by SCM (400 °C, 1 h).

Theoretical XRD pattern of $ZnGa_2O_4$ powders with spinel structure was shown in Fig. 2(a). The XRD pattern of Fig. 2(b) was obtained from SSRM $ZnGa_2O_4$ powders which were calcined at 1200 °C for 10 h. This pattern shows that the crystalline quality of SSRM $ZnGa_2O_4$ powders reached to the theoretical level. Fig. 2(c) shows small extra peaks which probably came from carbon remains formed during combustion. These were completely removed after calcined at 400 °C for 1 h as shown in Fig. 2(d). Fig. 2(d) shows that the crystalline quality of SCM $ZnGa_2O_4$ powders also reached to the theoretical level even though they were calcined at 400 °C for 1 h rather than at 1200 °C for 10 h.

As shown in Fig. 3, the average particle size of SSRM $ZnGa_2O_4$ powders was about 5 μm. However, that of SCM $ZnGa_2O_4$ powders was about 50 nm. This small particle size was probably due to the instantaneous high pressure explosion

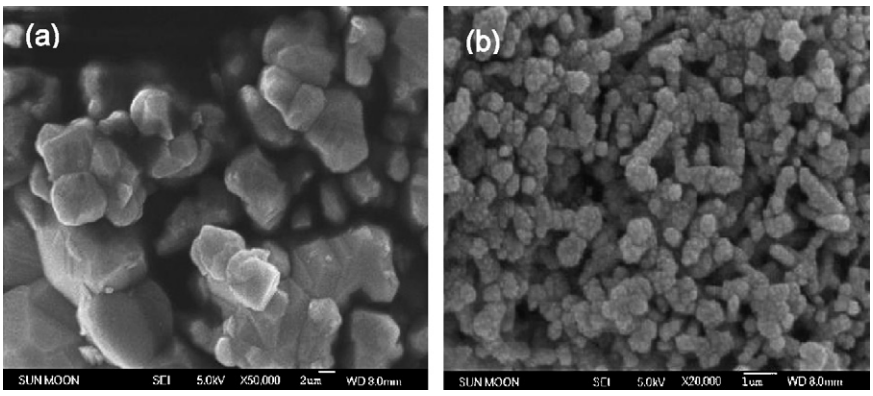

Fig. 3. SEM photographs of $ZnGa_2O_4$ powder (a) prepared by SSRM (1200 °C, 10 h) and (b) prepared by SCM (400 °C, 1 h).

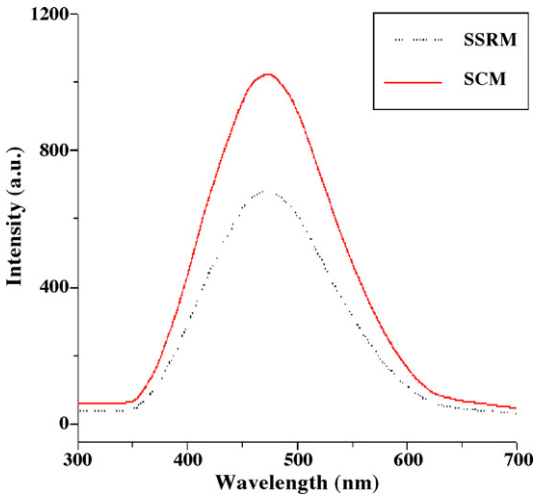

Fig. 4. Emission spectra of $ZnGa_2O_4$ powder.

during reaction. Based on BET measurement, the specific surface areas of both SSRM $ZnGa_2O_4$ and SCM $ZnGa_2O_4$ powders were 1.79 and 86.54 m^2/g, respectively.

PL emission spectra of both SSRM $ZnGa_2O_4$ and SCM $ZnGa_2O_4$ powders are shown in Fig. 4. Here a Xe lamp was irradiated on the powders. Both spectra were relatively broad ranging from 350 to 650 nm. They showed peaks at near 470 nm. The emission intensity (peaks at near 470 nm) of SCM $ZnGa_2O_4$ powders was about 1.5-fold higher compared to that of SSRM $ZnGa_2O_4$ powders. This might be mainly due to the large specific surface area that is 48-fold larger than that of SSRM $ZnGa_2O_4$ powders. Because the operation voltage in displays such as field emission displays is low, the penetration of electrons into the phosphor particle is very shallow. The low penetration of electrons into the particle means that emission from the phosphor must involve energy transfer within the shallow surface layer such as several 10 Å below the surface. It is clear that, at low voltages, the nature and perfection of the phosphor surfaces play an important role in the performance of phosphors. The large surface area, thus, could contribute to the high intensity. Furthermore, the surface perfection of SCM $ZnGa_2O_4$ powders might be very good because of its high instantaneous temperature during synthesis.

Fig. 5 represents XRD patterns of $Zn_{1-x}Mn_xGa_2O_4$ powders prepared by SCM. The added amount of Mn^{2+} ions was ranging from 0.001 to 0.012 mol fraction. The $Zn_{1-x}Mn_xGa_2O_4$ powders were heat-treated at 650 °C for 5 h. All the XRD patterns of $Zn_{1-x}Mn_xGa_2O_4$ powders were corresponding to that of pure $ZnGa_2O_4$ powders shown in Fig. 2(a). This means that the addition of Mn^{2+} ions did not change any crystalline structure. The added Mn^{2+} ions replaced the Zn lattice sites.

As shown in Fig. 6, the emission peak shifted from blue to green color when the Mn^{2+} ions were added to SCM $ZnGa_2O_4$ powders. The peaks were centered at near 513 nm for all cases. The green emission spectra probably came from the fact that Mn^{2+} ions replace tetrahedral Zn^{2+} sites rather than Mn^{4+} ions replace octahedral Ga^{3+} sites. The highest peak was obtained when the added amount of Mn^{2+} ions was 0.003 mol fraction. The peak was lowest when the added amount of Mn^{2+} ions was

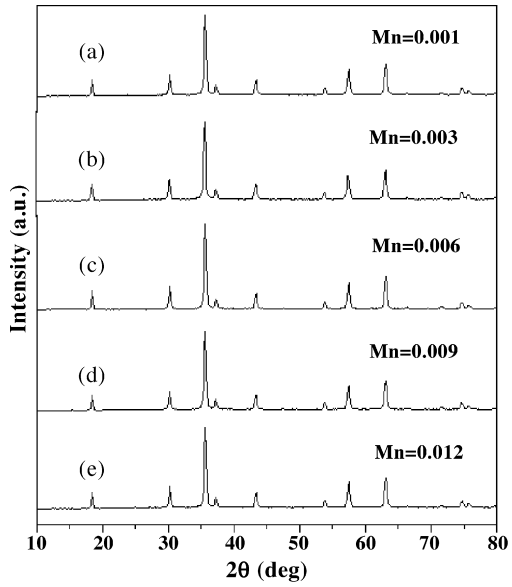

Fig. 5. XRD patterns of $Zn_{1-x}Mn_xGa_2O_4$ powder prepared by SCM.

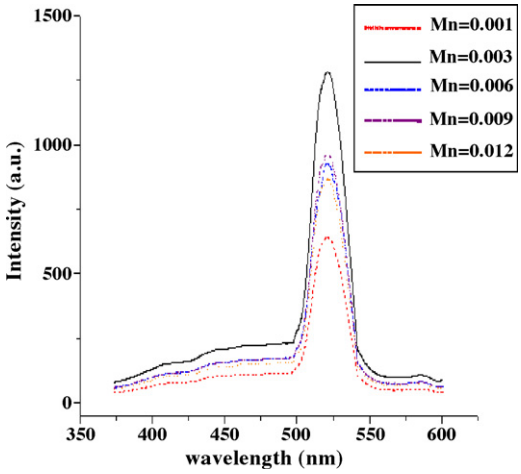

Fig. 6. Emission spectra of $Zn_{1-x}Mn_xGa_2O_4$ powders prepared by SCM with changing the added amount of Mn^{2+} ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

0.001 mol fraction. This means that the added amount of Mn^{2+} ions was not enough. It shows almost same peak height when Mn^{2+} ions of 0.006 and 0.009 mol fraction were added. The peak became lower with Mn^{2+} ions of 0.012 mol fraction. This indicates that the concentration quenching occurs if the Mn^{2+} ions are added more than 0.003 mol fraction.

4. Conclusion

The emission intensity (peaks at near 470 nm) of SCM $ZnGa_2O_4$ powders was about 1.5-fold higher compared to that of SSRM $ZnGa_2O_4$ powders. This might be due to the large specific surface area that is 48-fold larger than that of SSRM $ZnGa_2O_4$ powders.

The emission peak shifted from blue to green color when the Mn^{2+} ions were added to SCM $ZnGa_2O_4$ powders. The peaks

were centered at near 513 nm. The highest peak was observed with Mn^{2+} ions of 0.003 mol fraction. Furthermore, the spectra became sharper than those of pure $ZnGa_2O_4$ powders. This is more desirable for displays which use three pure color phosphors with red, green and blue colors.

In the design of phosphors for low voltage operations, there are three key factors to be considered, the morphology and size, the stoichiometry and composition, and the surface quality. It seems that the solution combustion method mostly satisfies these factors. This might be very useful for high efficiency and low voltage phosphors for displays such as field emission displays and plasma display panels.

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