

# Luminescence properties of ZnGa<sub>2</sub>O<sub>4</sub> based phosphors

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## Abstract

Phosphor powders of zinc gallate added with Mg and rare-earth elements were prepared by solid state reaction to improve luminescent properties. Green emitting ZnMnGa<sub>2</sub>O<sub>4</sub> reached maximum intensity at Mn=0.005 mole% and further improvement was achieved by addition of Mg<sup>2+</sup>. Tm, Mg-added zinc gallate phosphor exhibited a strong blue band emission, peaking at about 420 nm with the maximum intensity at the concentration of 0.003 mole% Mg and 0.015 mole% Tm. Deepening of the potential wells of the ground and excited states was suggested to be the cause for the enhancement in emission intensity at optimal doping of Mg and Tm.

## 1. Introduction

Phosphors materials have continued to attract much attention of researchers for their field emission display application. High resolution, short decay time, high brightness, and high efficiency are the major requirements of phosphors used in flat panel display devices such as field emission displays (FEDs)[1]. In this context, ZnGa<sub>2</sub>O<sub>4</sub> based materials, for example ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup>, are interesting, as they show reduced out-gassing and possess high chemical stability compared to the conventional sulfide phosphors. But the main short-coming with these materials is their low luminescence intensity, and luminescence from ZnGa<sub>2</sub>O<sub>4</sub> (blue) and ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup> (green) is not bright enough to get appreciation among researchers for field emission display applications. Hence, a huge amount of research has been oriented towards modification of ZnGa<sub>2</sub>O<sub>4</sub> to increase its emission property. For example mixing of oxides such as SnO<sub>2</sub> and InO<sub>3</sub> with ZnGa<sub>2</sub>O<sub>4</sub> enhanced the emission intensity [2]. Similarly Li doping also improved the emission characteristics [3-4]. Synthesis of the samples under reducing atmosphere [5] and excess Zn<sup>2+</sup>[6] also caused increased emission characteristics. In the present study it was examined the effect of isomorphous substitution of Zn by Mg<sup>2+</sup> in ZnGa<sub>2</sub>O<sub>4</sub>:Mn<sup>2+</sup> on the emission intensity. As both Zn and Mg only little differ in their ionic radii (0.074 and 0.072 nm respectively), Mg could be accommodated in the lattice of ZnGa<sub>2</sub>O<sub>4</sub>:Mn. In addition, the substitution might favourably deepen the potential well of both the ground and excited states so that the luminescence intensity could be enhanced. It is therefore quite logical to investigate the effect of Mg<sup>2+</sup> doping at the optimum Mn<sup>2+</sup> concentration on the photoluminescence properties.

In addition to achieve high green luminescence by substituting Zn<sup>2+</sup> by Mn<sup>2+</sup> and Mg<sup>2+</sup>, in ZnGa<sub>2</sub>O<sub>4</sub> lattice, it was also interest to modify blue light emitting host lattice ZnGa<sub>2</sub>O<sub>4</sub>. It showed a low intensity broad band, and therefore the improvement is required to enhance the intensity and color purity aspects. Rare earth doping especially Tm<sup>3+</sup>[7] is known to emit in the blue region of the spectrum. Tm with partially filled 4f shells, shielded by 5S<sup>2</sup> and 5P<sup>6</sup> electrons, is an ideal ion to obtain sharp emission lines (color purity) in a proper host. Therefore, it is reasonable to attempt phosphor synthesis by substituting Ga<sup>3+</sup> by Tm<sup>3+</sup> in blue emitting ZnGa<sub>2</sub>O<sub>4</sub> host.

## 2. Experimental Procedure

In the preparation of Zn<sub>1-x</sub>Ga<sub>2</sub>O<sub>4</sub>:Mn<sub>x</sub>, x was varied from 0.001-0.008 mole. For Mg substitution the optimum level of Mn with respect to emission intensity in ZnGa<sub>2</sub>O<sub>4</sub>:Mn was used. Rare earth

substitution in  $Zn_{1-x}Mg_x(Ga_{1-x}Re_x)$  where  $Re = Tm$  was carried out with optimum level of  $Tm$  (0.015 mol%) with different  $Mg$  level (0.1- 0.8 mol%). In each preparation, appropriate amounts of the starting materials in acetone were thoroughly mixed by grinding in an agate mortar, and the slurry was evaporated to dryness at 80°C. The powders were then sintered at 1200°C for 3 h in air, and fired in a reduction atmosphere of 95% $N_2$ -5% $H_2$  at 900°C for 1 hour with a flow of 50 mL/min.

The crystal structures of phosphor powders were investigated by Rigaku D/MAX-2200V X-ray diffractometer with  $CuK\alpha$  radiation. The photoluminescence (PL) emission and excitation spectra of powder samples were obtained using a Perkin-Elmer LS50B luminescence spectrometer. Each sample was loaded into a circular holder and excited with 254 nm radiation from a pulsed xenon lamp. The emission spectra were scanned in the wavelength range from 400-800 nm. To measure the excitation spectra, the analyzer monochromator was set to the maximum wavelength of the emission spectra and then an excitation monochromator was scanned in the range of 200-400 nm.

### 3. Results and Discussion

The XRD patterns of two compositions  $Zn_{0.995}Ga_2O_4:Mn_{0.005}$  and  $Zn_{0.99}Mg_{0.005}Ga_2O_4:Mn_{0.005}$  are shown in Fig.1. All other compositions showed similar patterns. Both samples display the spinel phase of  $ZnGa_2O_4$  having a cubic normal spinel crystal structure with  $Fd3m$  space group.

Fig. 2 illustrates the effect of  $Mg^{2+}$  concentration on the emission intensity of  $ZnGa_2O_4:Mn^{2+}$  phosphor. It is observed that the intensity of emission increases with increase in  $Mg^{2+}$  doping and reaches maximum at 0.005mol%. However, the emission decreases for further increase in concentration. These observations reflect the effect of  $Mg^{2+}$  substitution in the  $ZnGa_2O_4:Mn^{2+}$  lattice. The addition of  $Mg^{2+}$  might prevent such  $Mn^{2+}-Mn^{2+}$  energy transfer. Thus  $Mg^{2+}$  ions increase the number of effective active sensitizer ions. This explains the enhancement of the emission. The host matrix, as mentioned earlier in the text, is also optimized for  $Mn^{2+}$  doping for highest emission intensity. The concept is consistent to explain the decreasing emission intensity beyond optimum concentration of 0.005 mole  $Mg^{2+}$ . The mechanism of such process, as given by Ryu & Park [8], is that the probability of energy transfer by the sensitizers dominates over the emission process. The limited number of tetrahedral sites in spinel  $ZnGa_2O_4$  would be inevitably make sensitizer ion energy transfer inevitable after certain concentration of  $Mg^{2+}$  ions in the present study.

Figure 3 illustrates the decay curves of  $ZnGa_2O_4:Mn^{2+}$  as a function of  $Mg^{2+}$  concentration. The model proposed for  $Mg^{2+}$  effect on emission intensity also explains the observation of decay time studies. The features of the study are: (1) with increasing  $Mg$  concentration the decay time is lowered, (2) for optimum concentration with respect to emission i.e.  $Mg = 0.005$  mole%, the decay time is higher than the host sample. However the enhancement in decay time is only 5 to 6% which is insignificant with respect to application prospects. Morell et al[9] have reported that the formation of sensitizer pairs in the host can decrease the decay time. As explained in the emission studies earlier, the role of  $Mg$  is to avoid  $Mn^{2+}-Mn^{2+}$  interactions.

The excitation spectra of  $ZnGa_2O_4$  and  $Zn(Ga_{0.985}Tm_{0.015})_2O_4$  are shown in the Fig. 4. There is remarkable increase in the excitation intensity due to addition of  $Tm$ . This observation suggests well dispersion of  $Ga$  in the lattice by the addition of  $Tm$ , thus putting maximum number of  $Ga$  in the zone of excitation. More specifically addition of  $Tm$  can make the potential well of the ground state of zinc gallate to be very deep facilitating more of  $Ga-O$  bonds in their equilibrium inter-nuclear distance. This situation should also be applicable to the excited state in order to account for high excitation intensity. As  $Tm$  is a lanthanide, experiencing the influence of lanthanide contraction, its little addition to  $ZnGa_2O_4$  as a substitute for  $Ga$  provides better bonding property making thus the potential well a bit narrow.

The emission spectra of  $Zn(Ga_{0.985}Tm_{0.015})_2O_4$  doped with different level of  $Mg^{2+}$  are shown in Fig 5. The intensity increased with increase in  $Mg^{2+}$  loading from 0.1 to 0.3 mol%, but decreased above 0.3mole%. The broad blue emission is unequivocally assigned to  $ZnGa_2O_4$ , as the  ${}^1G_4-{}^3H_4$  transition of  $Tm^{3+}$  is shown to give narrow emission intensity [10]. Since  $Mg^{2+}$  can only substitute  $Zn^{2+}$  resting in the tetrahedral hole it can not have any direct influence on the emission property of  $Ga$ . But it can modify the bonding property of lattice sites, as there is little difference in the ionization

potential and ionic radius from Zn. Based on the more electropositive character of Mg than Zn, it can be said that the former can provide better bonding property for the lattice than the latter at a certain level of loading. As a result of this the equilibrium inter-nuclear distance of the excited state of Mg doped crystal up to 0.3 mol% may not deviate much from the ground state. This property, therefore, is expected to give enhanced emission property for lower loading of  $Mg^{2+}$ . But it can not be expected to have linear response in the emission with  $Mg^{2+}$  loading, as higher Mg loading above 0.3 mol% and in  $Mg(Ga_{0.985}Tm_{0.015})_2O_4$ , the potential well of the ground as well as the excited states may not be as deep as in optimally loaded  $Mg^{2+}$  crystals. Hence the excited state with broadened well is to give very broad band emission with less intensity as observed in this study. In addition at optimum level of Mg loading the defect state transitions could also be kept minimum for enhanced emission.

#### 4. Conclusion

From this study it is concluded that the green emission property of zinc gallate can be improved by increasing the Mg loading up to 0.008 mole% at a constant Mn loading of 0.005 mole%. The blue emission intensity of zinc gallate doped with Mg and Tm increased with increase in Mg loading up to 0.3mol%. These results are encouraging to take up further studies to obtain ideal green and blue emitting phosphors by the use of  $ZnGa_2O_4$  host.

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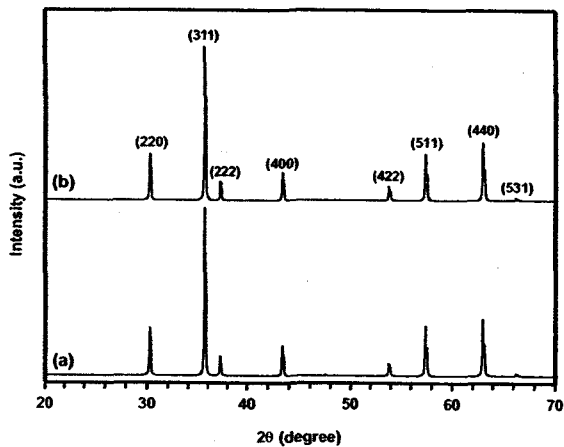


Fig.1 X-ray diffraction pattern of (a)  $Zn_{0.995}Ga_2O_4:Mn_{0.005}$ ; (b)  $Zn_{0.99}Mg_{0.005}Ga_2O_4:Mn_{0.005}$ .

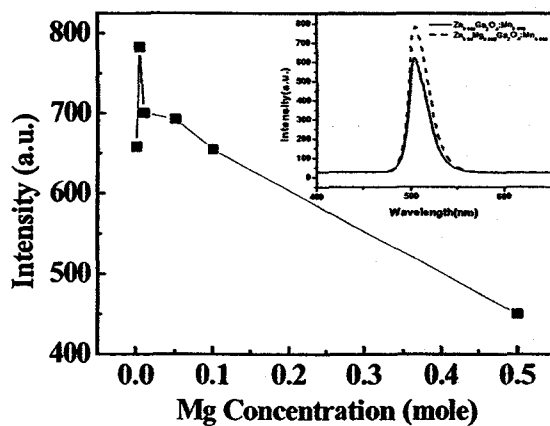


Fig.2 PL emission spectra of  $Zn_{0.995}Ga_2O_4:Mn_{0.005}$  doped with various amount of  $Mg^{2+}$ . The inset figure shows the effect of  $Mg^{2+}$  on the PL intensity

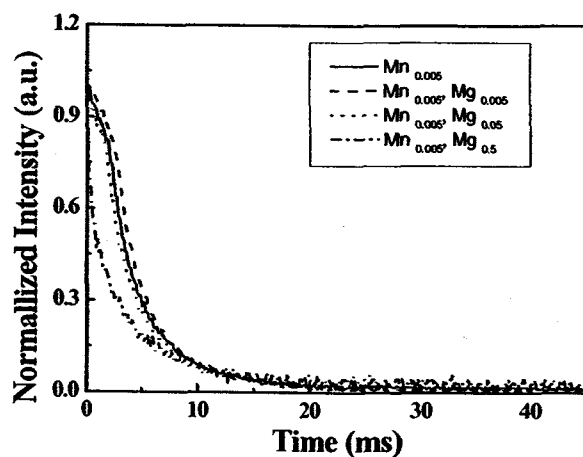


Fig.3 Decay curves for doped and undoped  $Mg^{2+}$  in  $Zn_{0.995}Ga_2O_4:Mn_{0.005}$ .

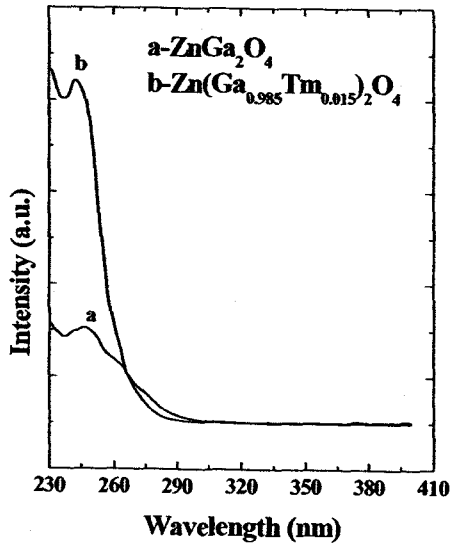


Fig.4 Excitation spectra of  $\text{ZnGa}_2\text{O}_4$  and  $\text{Zn}(\text{Ga}_{0.985}\text{Tm}_{0.015})_2\text{O}_4$ .

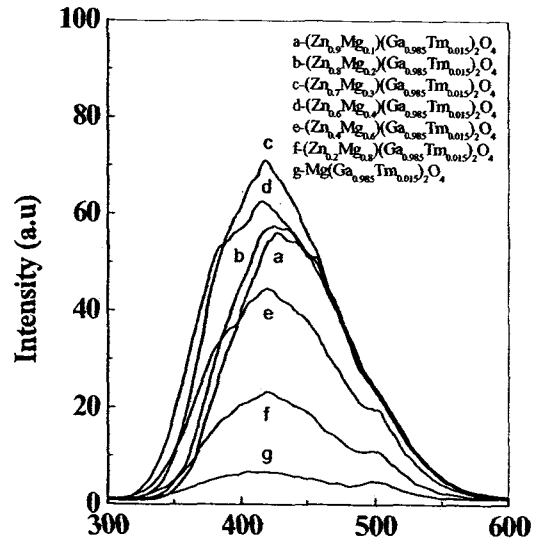


Fig.5 PL emission spectra of  $\text{Zn}(\text{Ga}_{0.985}\text{Tm}_{0.015})\text{O}_4$  as a function of Mg concentration.