



EFFECT OF DEPOSITION PARAMETERS ON Mn DOPED ZnGa₂O₄ PHOSPHOR DEPOSITED BY PLD

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ABSTRACT

ZnGa₂O₄:Mn phosphors have shown lot of promise because of their superior stability and excellent luminescence property compared to sulphide based materials. In this work ZnGa₂O₄:Mn was synthesised by a citrate gel method at a temperature of 1050°C by carbo-thermal reduction and gave emissions at 504 nm (excitation λ = 287 nm). The powder was pelletised and deposited as thin film by using Pulsed Laser Deposition (PLD) at different temperatures and photoluminescence was observed. Maximum luminescence was observed in the film deposited and annealed at 450°C. SEM images show finer grains in the film deposited on a glass substrate in comparison to a quartz substrate, resulting in enhanced luminescence intensity.

Key words: Luminescence, Zinc Gallate, Thin film, PLD

1. INTRODUCTION

In recent years lot of research has been done on the development of luminescent materials for next generation flat panel display devices like Field Emission Displays (FEDs), Vacuum Fluorescence Displays (VFDs), Electroluminescent display panels etc. Various sulphide phosphors have been explored for the purpose. But their major drawback remains the following¹⁻³.

- (a) Volatility of sulphur, which prohibits its use in FEDs or VFDs.
- (b) Under the influence of high-energy electrons the cation-sulphur bond tends to dissociate.
- (c) Sulphur bearing gas is corrosive in nature and contaminates the emission tips and shortens the device life.

On the other hand oxide phosphors exhibit much superior stability and excellent luminescence property.

Luminescence of ZnGa₂O₄:Mn has been studied by various researchers and emission peaks of this material has been reported to be from 501nm⁴ to 506 nm^{5,6}. Activation of Mn²⁺ ions causes luminescence by a ⁴T₁-⁶A₁ transition between 3d electrons within the Mn²⁺ ion⁷. It is assumed that Mn²⁺ ions replace Zn²⁺ ions in the host lattice because of the same valancy. However, during doping of ZnGa₂O₄ phosphors, Mn²⁺ can get oxidised to Mn⁴⁺ and faint orange green light appears at 666 nm⁸. In order to prevent the oxidation of Mn²⁺, firing is generally done in a protective atmosphere of Ar⁹ or in vacuum⁶. Some researchers have produced these phosphors successfully by initial sintering in air and subsequent reduction in H₂ atmosphere¹⁰. Solid state methods are quite commonly used for production of these phosphors. However, solid state routes require high temperature processing (1200-1300°C) for prolonged periods as much as 12

hours. Surprisingly, very little work has been done on synthesising this material by other low temperature routes like sol gel, coprecipitation etc¹¹.

In this work Mn^{2+} doped Zinc gallate powder was prepared by a citrate-gel method. In addition to greater homogeneity and purity of the product, the citrate gel method allows for a lower processing temperature with greater morphological control. This method involves the formation of a mixed ion citrate that forms three-dimensional network upon drying (gel). Subsequent pyrolysis of the gel yields a homogeneous mixed oxide¹².

Although thin film phosphors have several advantages compared to powders, such as higher lateral resolution from smaller grains, better thermal stability, reduced outgassing, and better adhesion to the solid surface, it is also essential that the substrate should possess good optical properties in terms of low absorption and high transmittance of the generated light. There have been few studies involving epitaxial luminescent film⁸. In this study optimisation of the substrate temperature during Pulsed Laser Deposition has also been carried out.

2. EXPERIMENTAL

$ZnGa_2O_4:Mn$ powder was prepared by a citrate gel method. Ga_2O_3 (99.999% pure), ZnO (99.999% pure) and $MnSO_4 \cdot H_2O$ were dissolved in a 3:1 mixture of HCl and HNO_3 under constant stirring till a clear solution was obtained. Following this an appropriate amount of citric acid was added such that molar ratio of the metal ions to the citric acid was 1:1.2. The mixture was heated to a temperature of $130^\circ C$ and stirred till a yellowish-green semitransparent gel was obtained. This gel was dried in an oven at a temperature of $180^\circ C$ and subsequently heated to $600^\circ C$ in air for 5 hours. The resultant powder was fired in a carburising atmosphere at a temperature of $1050^\circ C$. Luminescence of the final powder was characterized. The powder was pelletised and sintered at $950^\circ C$ for 5 hours. Thin film was deposited using pulsed laser deposition, on quartz and glass substrates. Table-1 gives the deposition parameter.

Characterization of thin film was done using XRD and SEM. The photoluminescence spectra were obtained using a fluorescence spectrophotometer.

3. RESULTS AND DISCUSSIONS

XRD pattern of the powder (Figure 1) confirmed the formation of the $ZnGa_2O_4$ phase by carbo-thermal reduction at $1050^\circ C$. Some smaller peaks near 2θ values of 32° and 54° were due to the presence of a small amount of excess Ga_2O_3 . This was attributed to the loss of ZnO on heating at $1050^\circ C$.

AUTOX[®] fitting of the XRD data that gave excellent fit and a lattice parameter of 8.316 \AA , as reported by earlier researchers^{6,12}, was obtained. This compound gave luminescence at 504 nm . Compounds having 1:1 and 1.1:1 molar ratio of ZnO/Ga_2O_3 showed luminescence at 504 nm when excited by the wavelength of 287 nm (Figure 2). This green emission was attributed to d-d transition ($^4T_1-^6A_1$) in the Mn^{2+} ion in tetrahedral sites. Sintering at higher temperatures led to ZnO loss (as indicated by presence of excess Ga_2O_3 peak in the XRD pattern) and was compensated by an excess molar ratio of ZnO . This was the reason that the 1.1:1 molar ratio of ZnO/Ga_2O_3 showed higher emission intensity (Figure 2).

The thin film thickness (after deposition by PLD) was measured using ellipsometry. The thickness was estimated to be 1000 \AA and the refractive index was 3.4. XRD patterns of the thin films deposited at different temperatures are depicted in figure 3. At a deposition temperature of $450^\circ C$ only the peaks corresponding to $ZnGa_2O_4$ (311) are seen. On the other hand at the higher temperatures of $550^\circ C$ and $700^\circ C$, peaks of Ga_2O_3 are evident, which becomes stronger as the

temperature increases which indicates that ZnO evaporates progressively as temperature increases.

In thin film form there are two competing factors that affect the luminescence. One is crystallinity of the deposited compound, which increases with temperature and the other is the loss of ZnO. Evaporation of ZnO affects the luminescence adversely while good crystallinity of the compound is essential for luminescence in $\text{ZnGa}_2\text{O}_4\text{:Mn}$. It can be seen from excitation and emission spectra of these films (Figure 4 and 5) that luminescence intensity initially increased on increasing the deposition temperature, from 350° to 450° C, but at temperatures higher than 450°C the intensity came down. Highest emission intensity was observed at a deposition temperature of 450°C. At 700°C emission intensity at 503 nm was very low. However, the emission intensity at a wavelength of 365 nm (Figure 4) got more pronounced with increase in deposition temperature and was maximum for the film deposited and annealed at 700°C. It has been observed that when ZnGa_2O_4 is synthesised in oxygen deficient atmosphere where Zn^{2+} site vacancy gets created due to loss of ZnO, Ga^{3+} does not necessarily remain confined to octahedral sites and some of it goes to the goes to tetrahedral sites.

Presence of Ga_2O_3 in tetrahedral sites gives luminescence peak at 360 nm¹³. In this study, the emission at 365 nm was attributed to the presence of excess Ga^{3+} ions, occupying the tetrahedral sites. Blue luminescence near the wavelength of 430 nm in the emission spectra was because of host emission.

There was no difference in the emission wavelength of the films deposited on quartz and ITO coated glass substrates. However, slight reduction in intensity was observed in the films deposited on quartz substrates (Figure 5), which was because of smaller grains in the thin film deposited on glass. This is evident from the SEM images depicted in Figure 7.

4. CONCLUSIONS

$\text{ZnGa}_2\text{O}_4\text{:Mn}_{0.01}$ powder was successfully synthesised by a citrate gel method followed by firing at temperature much lower than that required by traditional solid state reaction methods. The luminescence characteristics strongly depended on the ZnO: Ga_2O_3 molar ratio present in the compound and emission was obtained at 504 nm. The optimum substrate temperature for thin film deposition of $\text{ZnGa}_2\text{O}_4\text{:Mn}$ by PLD was 450°C at an oxygen pressure of 100 mTorr, with an annealing time of 30 minutes at the same temperature. At temperatures below 450°C crystallinity (and, therefore the luminescence) was poor and at higher temperatures loss of ZnO led to reduced luminescence. For the same conditions of deposition, the luminescence intensity of film deposited on (ITO coated) glass substrate was better than on quartz.

5. REFERENCES

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Table-1 PLD Parameters for Deposition

Laser Fluence	2.2 J/ cm ²
Wavelength	355 nm
Spot size	1 mm ²
Pulse Repetition Rate	19 ns
Vacuum level obtained before introducing Oxygen	1 * 10 ⁻⁵ Torr
Oxygen Partial Pressure	0.1 Torr
Temperature of the substrate deposition	350°C, 450°C, 550°C, 700°C
Annealing Temperature	350°C, 450°C, 550°C, 700°C
Annealing Time	30 min for all substrates

FIGURES

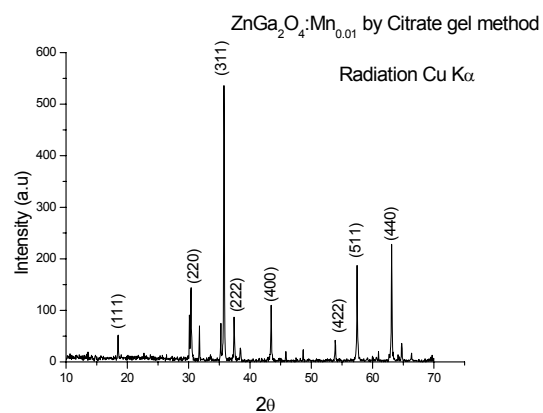


Figure1. XRD of $\text{ZnGa}_2\text{O}_4:\text{Mn}_{0.01}$ prepared by citrate gel method

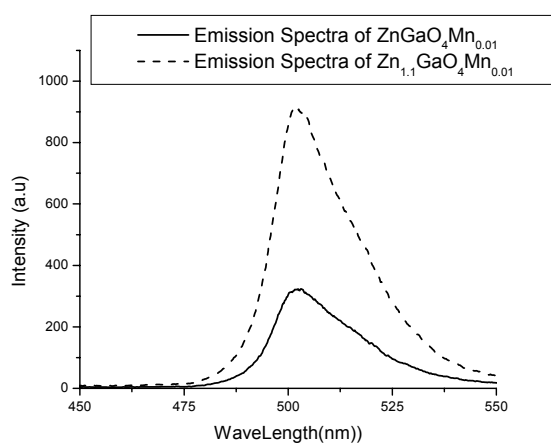


Figure 2. Emission Spectra of $\text{Zn}_{1.1}\text{Ga}_2\text{O}_4:\text{Mn}_{0.01}$ and $\text{ZnGa}_2\text{O}_4:\text{Mn}_{0.01}$ synthesized by citrate gel method

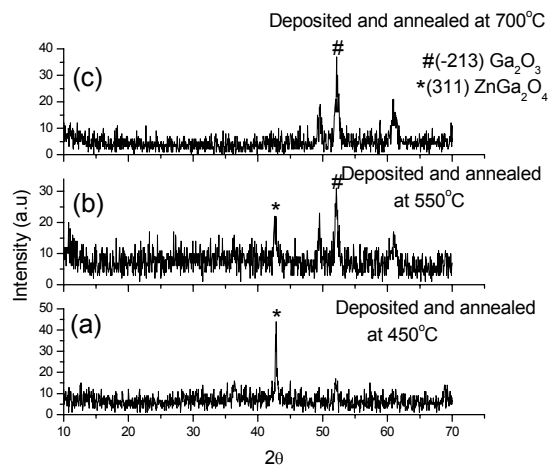


Figure 3. XRD (Co K α Radiation) pattern of the film deposited at (a) 700°C, (b) 550°C (c) 450°C

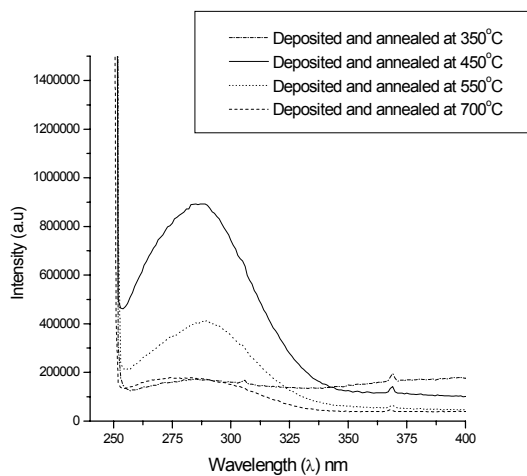


Figure 4. Excitation spectra of ZnGa₂O₄:Mn_{0.01} thin films deposited and annealed at different Temperatures

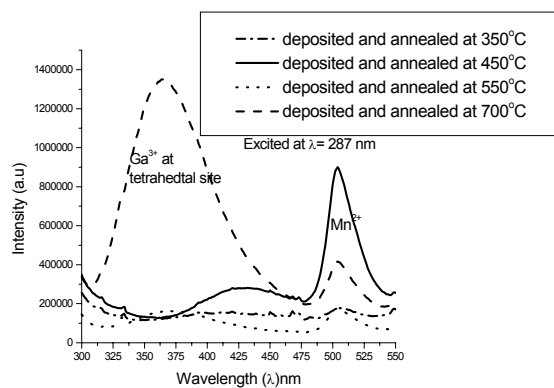


Figure 5. Excitation spectra of $\text{ZnGa}_2\text{O}_4:\text{Mn}_{0.01}$ thin films deposited and annealed at different Temperatures.

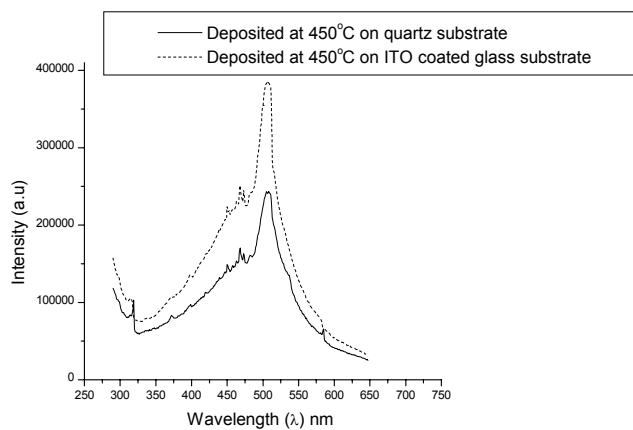


Figure 6. Emission spectra of thin film $\text{ZnGa}_2\text{O}_4:\text{Mn}_{0.01}$ deposited at 450°C over different substrate.

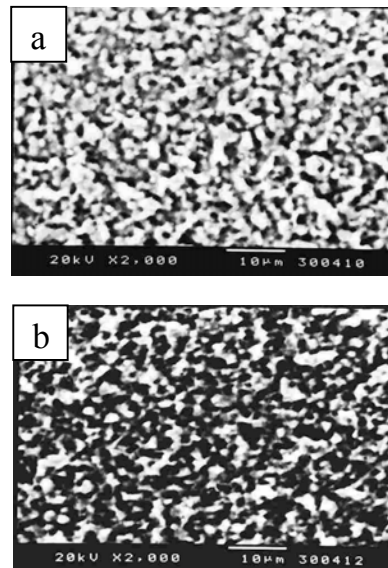


Figure 7. SEM image of thin film deposited on (a) Quartz, (b) Glass substrate at 450°C and annealed for 30 minutes at the same temperature