

Effect of Mg²⁺ co-doping on luminescent properties of ZnGa₂O₄:Mn²⁺

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ABSTRACT

Zinc gallate, ZnGa₂O₄:Mn²⁺ co-doped with different concentrations of Mg²⁺ (0.001- 0.5 mol%) was prepared by solid state synthesis method. These compositions were investigated for their photoluminescence and cathodoluminescence properties. The optimized composition Zn_{0.990}Mg_{0.005}Ga₂O₄:Mn_{0.005} shows higher luminescence intensity compared to the parent phosphor. The intense green emission peak was found at 504 nm. The Mg²⁺ doping does not affect much the decay time. It remains <10 ms for these compositions which make them potential candidate for application in TV screens.

Key Words : Phosphor, Solid state reaction, X-ray diffraction, SEM, Luminescence

1. INTRODUCTION

Phosphor materials having bright luminescence at low accelerating voltage are much in demand for various applications. Luminescence properties of spinel structure oxides with Mn or Cr doping are well studied. These phosphor materials have gained significant attention because of their diversified applications in field emission display[1]. High resolution, short decay time (preferably 1 to 5 ms), appreciable brightness and better stability are essential requirements for such applications. Sulfide based phosphors such as ZnS:Cu, Al and Y₂O₂S:Eu³⁺[2] possesses good cathodoluminescence properties, however, their chemical stability due to release of acidic fumes over a period of time are the major concerns. Zinc gallate, ZnGa₂O₄:Mn²⁺ exhibits interesting characteristic features with less out gassing and high chemical stability and therefore, are potential candidates for FED and vacuum fluorescent display[3]. Photoluminescent intensity of these materials is found low with broad emission spectrum. To overcome these shortcomings, efforts have been made towards the modification of ZnGa₂O₄ lattice with SnO₂, InO₃ [4, 5] and Li⁺ dop-

ing [6, 7]. Reducing atmosphere [8] doping of Si⁴⁺ [9] and excess of Zn²⁺ [10] were also found to enhance their emission characteristics. It is well known that the valence state of the activator dictates the emission wavelength [11]. Similarly the trivalent Eu³⁺ ions show red luminescence properties in highly stable lead based heavy metal oxide glasses [12].

In order to achieve better emission characteristic in the zinc gallate based phosphor materials, we have investigated the effect of Mg²⁺ doping with varying concentrations (0.001-0.5 mol%). Since both Zn²⁺ and Mg²⁺ have nearly same ionic radius (0.074 nm and 0.072 nm), it is expected that isomorphic substitution of Zn²⁺ with Mg²⁺ cause minimal variation in crystal lattice of ZnGa₂O₄ while enhancing its photoluminescence properties.

2. EXPERIMENTAL DETAILS

Parent zinc gallate, Zn_{1-x}Ga₂O₄:Mn_x and Mg co-doped Zn_{0.995-y}Mg_yGa₂O₄:Mn_{0.005} phosphors were prepared by solid state reaction technique. High purity (Aldrich, 99.999%) materials ZnO, MnO, MgO and Ga₂O₃ were used for preparation of the charge. In order to optimize the Mn²⁺ concentration for high emission intensity, it was varied from 0.001 to 0.008 mol %. Appropriate amount of the starting

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materials were thoroughly mixed in acetone in an agate mortar. The resulting slurry was dried at 80°C and then sintered at 1200°C for 3h in air atmosphere. Subsequent firing was done at 900°C for 1h in a reducing atmosphere of 95% Ar and 5% H₂ at a flow rate of 50 ml/min. Similar procedure was adopted for the preparation of Zn_{0.995-y}Mg_yGa₂O₄:Mn_{0.005} phosphor with different concentration of Mg²⁺ where, y varying from 0.001 to 0.5 mol%. The concentration of Mn²⁺ was kept constant at 0.005 mol %.

Phase and crystallinity of the synthesized compositions were investigated by powder XRD using Rigaku D/MAX-2200V diffractometer with Cu K_α radiation. The photoluminescence (PL) emission and excitation spectra were done on Perkin-Elmer LS50B luminescence spectrophotometer. 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 range of wavelengths from 400 to 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 to 400 nm. The cathodoluminescence was monitored by CL spectrometer using an electron beam with the excitation voltage of 800 V and the current of 40 μA. The decay curves were recorded using a pulsed Xenon lamp and oscilloscope.

3. RESULTS AND DISCUSSION

ZnMgGa₂O₄:Mn²⁺ compositions with varying concentrations of Mn²⁺ and Mg²⁺ were synthesized. The Mn²⁺ concentration in ZnGa₂O₄ was optimized independently. It was found that the Mn²⁺ concentration of 0.005 mol % is good for better luminescent properties. The optimized Mn²⁺ concentration of 0.005 mol % was kept constant while Mg²⁺ doping was optimized from 0.001 – 0.5 mol%. Fig. 1 shows the representative XRD pattern for the undoped and 0.005 mol% Mg doped ZnGa₂O₄:Mn²⁺. XRD patterns show that the material is having cubic spinel structure with Fd3m space group. Doping of Mg²⁺ does not show any detectable changes in the crystal lattice as the doping concentration is very small. Also the size of

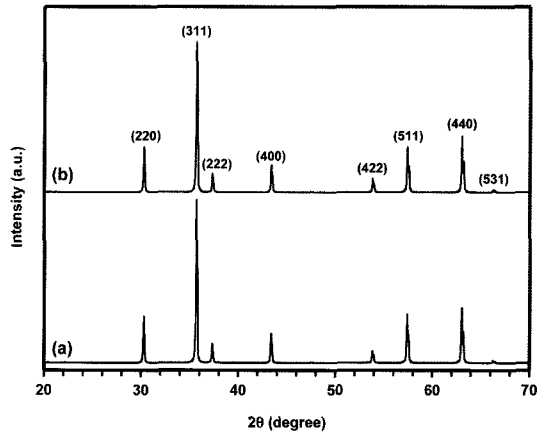


Fig. 1. XRD patterns for (a) Zn_{0.995}Ga₂O₄:Mn_{0.005}, (b) Zn_{0.99}Mg_{0.005}Ga₂O₄:Mn_{0.005}.

Mg²⁺ (0.72) is comparable to that of Zn²⁺ (0.74).

Fig. 2 shows variation in emission intensity of ZnGa₂O₄:Mn²⁺ with Mg²⁺ doping concentration. With increasing Mg²⁺ concentration up to 0.005 mol %, the intensity of emission increases. A further increase in Mg²⁺ concentration lowers the emission intensity, such lowering can occur because of nonradiative energy transfer of the Mn²⁺ ions. Mn²⁺ ion has an emission which consists of a broad band, the position of which depends strongly on the host lattice. Mn²⁺ doped zinc gallate is a low voltage cathodoluminescent green emitting phosphor, whose luminescence centers are Mn²⁺ ions (activators) in the tetrahedral sites of the crystal lattice. The green emission peak at 504 nm is due to the ⁴T₁–⁶A₁ transition of Mn²⁺ ions. The color dependence of the transition band is due to the host lattice and the crystal field [13]. The tetrahedrally coordinated Mn²⁺ is due to the weak crystal field, gives the green color emission. The host sensitized energy transfer is an important process in technological applications for luminescent materials, such as red emitting phosphor Eu³⁺: YVO₄. The peak at 245 nm represents absorption of the host ZnGa₂O₄ in particular, the Ga-O group (or Ga³⁺ ion), and the excitation energy was transferred in a nonradiative way from the host lattice (acting as sensitizer) to Mn²⁺ center (activator), followed by the green luminescence [14].

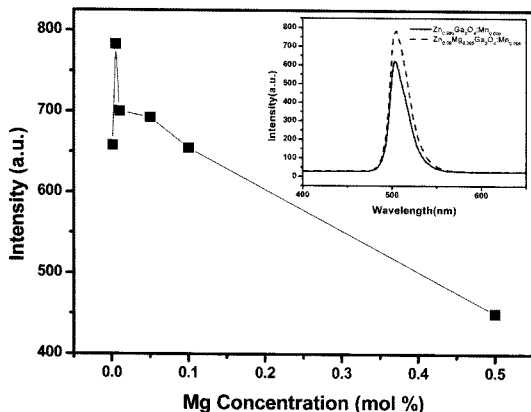


Fig. 2. Maximum intensity of PL spectra for Zn_{0.995}Ga₂O₄:Mn_{0.005} with varying Mg²⁺.

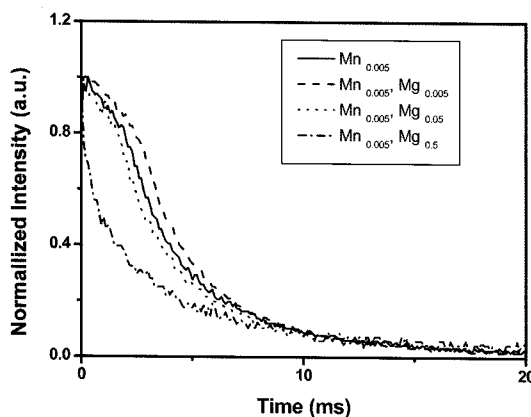


Fig. 3. Decay curves for undoped and Mg²⁺ doped Zn_{0.995}Ga₂O₄:Mn_{0.005}.

The inset in Fig. 2 shows the increase in peak emission intensity for 0.005 mol% Mg doped sample. However, beyond this concentration of Mg²⁺ (0.005 mol %) there is a decrease in emission. The limited number of tetrahedral sites in spinel ZnGa₂O₄ would make sensitizer ion energy transfer inevitable after certain concentration of Mg²⁺ ions [15]. The broad band in blue region around 400 nm in the spinel structure is due to the energy relaxation in the host lattice. This is what is observed in the parent phosphor composition. Whereas, it was absent in the case of 0.005 mol% Mg doped composition. It is due to the fact that the Mg doping up to certain critical concentration facilitate the efficient Mn²⁺ ion charge transfer to the host.

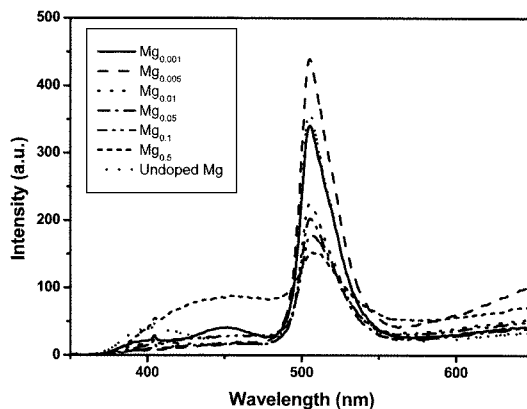


Fig. 4. The effect of Mg²⁺ doping on the cathodoluminescence properties of Zn_{0.995}Ga₂O₄:Mn_{0.005}.

Decay time of the luminescence spectra depends on the spin selection rule of the activator ion. Fig. 3 shows the time dependence of luminescence intensity measured after UV irradiation for ZnGa₂O₄:Mn²⁺ with varying Mg²⁺. The decay time for Mg doped samples does not increase as was expected due to increasing trap centers. When the spinel structure ZnGa₂O₄:Mn²⁺ is excited by the UV light, the mechanism responsible for the transfer of energy is the transfer from host to Mn²⁺ ions due to recombination of donor and acceptor ions. For TV screen applications, the decay time of the phosphors must be within few milliseconds. Since for higher decay time the images are got superimposed on the TV screen. Therefore, the compositions with decay time less than 10 ms are found potential candidates for TV screen applications.

The cathodoluminescence (CL) spectra of the parent ZnGa₂O₄:Mn²⁺ and its Mg²⁺ doped samples are shown in Fig. 4. The parent phosphor exhibits two emission bands; an intense low energy green emission band at 504 nm and a weak high energy broad blue emission band at ~400 nm. The green emission band is assigned to ⁴T₁–⁶A₁ transition of Mn²⁺ ions while the blue arises from the radiative recombination of delocalized charge carriers (electrons) with trapped charge carriers (holes).

The minor peak at higher energy occurs from the emission by the ZnGa₂O₄:Mn²⁺ host lattice. It is understood that the crystalline defects are caused due

to small ZnO evaporation in the parent lattice of $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$ while processing at high temperatures. However, small Mg^{2+} doping prevents ZnO formation and hence controls the crystalline defects. In this situation the energy absorbed by the lattice is transferred efficiently to Mn^{2+} . This is reflected in the enhanced emission of the green band. This is what is expected in the sample with $\text{Mg}^{2+}=0.005$ mol % to show higher emission. Noticeably the blue emission band is totally absent for Mg^{2+} for 0.005 mol%, contributing to efficient energy transfer to Mn^{2+} .

4. CONCLUSIONS

Phosphor compositions with varying concentrations of Mg were successfully made by solid state reaction technique. XRD results confirm the formation of single phase material. No effect of small doping concentration of active ions was observed in XRD results. PL spectra of 0.005 mol% of Mg^{2+} doped $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$ show significant enhancement in luminescent intensity. Mg^{2+} doping reduces the formation of ZnO, hence the reduction in defect centers in the crystal lattice. The intensity of the green emission in cathodoluminescence increases as a result of Mg^{2+} substitutions with the reduction in blue emission bands. The optimum Mg^{2+} substitution (0.005 mol %) in $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$ was found beneficial for enhancement in the luminescence intensity without any reduction in decay time (< 10 ms).

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