Chapter 3

Hydrothermal synthesis and characterization of undoped and Eu doped ZnGa$_2$O$_4$ nanoparticles

3.1 Introduction

Phosphors are substance that exhibits the phenomenon of luminescence. Efficient phosphors for lighting applications, flat panel displays, etc have always been a goal for researchers. Phosphor materials are generally composed of a pure host matrix and a small amount of intentionally added impurity, so-called activator [54]. If the host material and the activator concentrations are fixed, the physical properties of phosphor materials such as the surface area, the crystallinity, the phase purity, and the distribution of activator in the host matrix play crucial roles in modulating luminescence
characteristics. Those material properties can be controlled by the preparation conditions: temperature, precursor concentration, and post annealing. Especially, the preparation and annealing temperatures greatly influence the luminescence intensity of phosphor particles since it directly affects the formation of crystal structure, crystallinity, the surface area of particles, and the distribution of activator. \((\text{Y,Gd})\text{BO}_3:\text{Eu} [178]\) or \(\text{Y}_2\text{O}_3:\text{Eu} [179]\), \(\text{Zn}_2\text{SiO}_4:\text{Mn} [180]\), and \(\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu} [181]\) are some phosphor materials which give red, green and blue emission respectively. Generally, most of the light emitting devices utilizes red, green, and blue colors for practical applications. The particle size of conventional phosphors are in micrometer scale, hence light scattering at grain boundaries is strong and it decreases the light output. Nanophosphors can be synthesized whose size varying from tens to hundreds of nanometers which itself are smaller than the incident light wavelength and this will reduce the scattering, thereby enhancing the luminescence efficiency. Synthesis of nanometre-size phosphors has attracted much attention owing to their size-dependent electrical and optical properties originating from the quantum confinement.

Zinc gallium oxide, \(\text{ZnGa}_2\text{O}_4\), is a well-known low voltage oxide phosphor used in flat panel displays [182–184]. This ternary oxide compound is a self activated phosphor, crystallizing in the normal spinel structure. The spinel unit cell belongs to the cubic space group Oh7 (Fd\(_{3m}\)) with eight formula units per cell and contains two kinds of cation sites. The A site (\(\text{Zn}^{2+}\)) has tetrahedral coordination with full T\(_d\) symmetry, while the B site (\(\text{Ga}^{3+}\)) has six fold distorted octahedral coordination belonging to the D\(_{3d}\) point group. The trigonal axis of the B site is, of course, coincident with the unit cell (111) axis, and the site has a center of inversion [185]. When undoped, \(\text{ZnGa}_2\text{O}_4\) provides a blue emission and rare earth doping
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gives the emission characteristics of rare earth ions and provides tunability over the whole visible spectra. Therefore zinc gallate is an excellent multi color phosphor material for flat panel displays. White light emitters have attracted special interest recently for a number of potential applications in cars, traffic information signs, displays and general illumination [132–134]. White LEDs can be fabricated by several methods [133]. The first lies solely on combinations of LEDs with the three primary colors to produce bright white light sources which are significantly more efficient than incandescent bulbs and are more adaptable. Multiple semiconductor LEDs will not be competitive in the larger market for residential and commercial lighting. Moreover, the directional nature of LED output makes this approach not suitable for general illumination application. Another more practical method for producing white LEDs is upon absorption of blue or UV light, the phosphors convert the energy to visible radiation depending on the type of phosphors used. White light can be achieved either through several different colored phosphors, or utilizing the blue emission of the LED as the blue part of a multichromatic source. Ce$^{3+}$ doped Y$_3$Al$_5$O$_{12}$ nanophasor absorbs light efficiently in the visible region of 400-500 nm, and shows single broadband emission peaking at $\sim$560 nm and hence, it can be considered as a candidate for generating white light when coupled to a blue light-emitting diode [186].

Synthesis of ZnGa$_2$O$_4$ spinel powders have been previously accomplished by solid state reaction between zinc oxide and gallium oxide or by flux method [106, 109, 184, 187–189]. But this method requires heat treatment at higher temperatures for several hours and subsequent grinding. This may damage the phosphor surfaces, resulting in the loss of emission intensity. Various chemical syntheses have been developed to grow nanoparticles of
such ternary oxide materials [185, 190]. Hydrothermal method offers some advantages over the other techniques, such as low temperature synthesis, low cost, less hazardous and no need for the use of metal catalysts [190–192]. Hirano et al. [192] studied the growth of undoped ZnGa$_2$O$_4$ nanoparticles by hydrothermal method. Tas et al [193] prepared pure and Mn$^{2+}$ doped ZnGa$_2$O$_4$ nanoparticles by aging aqueous solutions of precursors and Takesada et al. [194] by glycothermal method. The effect of rare earth doping in the ZnGa$_2$O$_4$ spinel structure is less studied.

In the present study, undoped and Eu doped zinc gallium oxide (ZnGa$_2$O$_4$) nanoparticles were synthesized via hydrothermal route using metallic precursors. The effect of temperature, Zn/Ga precursor ratio, dopant concentration and duration of growth on the structural and optical properties of nanoparticles were studied.

### 3.2 Experimental

Fine powder of pure and Eu doped ZnGa$_2$O$_4$ phosphors were prepared by the hydrothermal method. High-purity metals of gallium (99.9999%, Alcan Electronic Materials) and zinc (99.995%, 5 mm dia, Qualigens) were dissolved in nitric acid (70%, Merck) separately and then diluted to appropriate concentrations with distilled water. The concentrations of the stock solutions were determined by inductively coupled plasma atomic emission spectrometric (ICP-AES) analysis (8440 PLASMALAB, LABTAM). The concentration of the gallium and zinc precursor solutions was determined to be 7.82 and 67.63 gm/litre respectively. The gallium and zinc stock solutions were mixed in the 1:2 volume ratios with constant stirring. To prepare ZnGa$_2$O$_4$:Eu$^{3+}$ phosphor, appropriate amount of Eu$_2$O$_3$ (99.99%,
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Alfa Aesar) was added to the mixed solution of parent cations. On constant stirring, a desired amount of aqueous ammonia (25%, Merck) was added to the clear solutions soon after dissolution to make pH of the solution as 8. The mixed solution was refluxed at room temperature in a magnetically stirred reactor for 30 minutes and then transferred into a teflon lined stainless steel autoclave. The tightly sealed autoclave was placed in oven and heated to a temperature of 200°C for 3 h under autogenous pressure. The precipitates, which were formed under autogenously established hydrothermal conditions, were separated by filtering, then washed and dried in air at 50°C in air. The samples were washed with H₂SO₄ so as to remove the residual ZnO phase, if any, present in them to obtain single phase zinc gallate spinel particles.

Phase identification of the fine white zinc gallate powders was performed by x-ray powder diffraction (XRD) (Rigaku D max-C) using Cu-Kα radiation (1.5418 Å). The morphology and size were examined by JEOL JEM-3100F transmission electron microscope (TEM) operating at 200 kV. The sample for TEM was prepared by placing a drop of the synthesized powder suspension in methanol onto a standard carbon coated copper grid. The grids were dried before recording the micrographs. The elemental composition of Eu in the synthesized powders was determined by using 8440 PLASMALAB, LABTAM inductively coupled plasma atomic emission spectrometer (ICP-AES). Thermogravimetric analysis (TGA) (Perkin Elmer) of the as prepared sample was carried out in the temperature range 50-1000°C at a heating rate of 10°C/min under nitrogen atmosphere. Horiba Jobin Yvon Fluoromax-3 spectrofluorimeter was used to investigate the photoluminescence properties of the phosphors at room temperature using Xe lamp as
the excitation source. FT-IR (Thermo Nicolet) spectra were recorded in the range 4000-400 cm$^{-1}$.

### 3.3 Results and discussion

![XRD pattern](image)

**Figure 3.1:** XRD pattern of (a) ICSD of ZnGa$_2$O$_4$ (ICSD Card No. 081113) (b) bulk ZnGa$_2$O$_4$ (c) ZnGa$_2$O$_4$ nanoparticles (d) Eu doped ZnGa$_2$O$_4$ nanoparticles

Figure 3.1 shows the XRD pattern of the ZnGa$_2$O$_4$ bulk powder (curve (b)) synthesized via solid state reaction by firing the mixture of ZnO and Ga$_2$O$_3$ at 1200$^\circ$C for 12 h. Curve (c) and (d) in figure 3.1 shows the XRD patterns of pure ZnGa$_2$O$_4$ and Eu doped ZnGa$_2$O$_4$ nanoparticles synthesized by hydrothermal technique at a growth temperature of 200$^\circ$C for 3 h. All the peaks in the x-ray diffraction pattern could be assigned to the typical spinel structure of ZnGa$_2$O$_4$ (Figure 3.1(a)) [195]. There
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are no characteristic peaks of constituent oxides regardless of the dopant concentrations. Thus the spinel structure is not modified by the addition of Eu into the ZnGa$_2$O$_4$ matrix. The broadening of the diffraction peaks shows that the synthesized materials are in nanometer regime.

Figure 3.2: XRD pattern of Eu doped ZnGa$_2$O$_4$ nanoparticles synthesized at various volume ratios of Zn/Ga precursor solutions at 200°C for 3 h
Undoped and Eu doped ZnGa$_2$O$_4$ nanoparticles

Figure 3.3: XRD pattern of Eu doped ZnGa$_2$O$_4$ nanoparticles synthesized at various temperature and duration of hydrothermal growth for a fixed volume ratio of 2 between Zn/Ga precursor solution.

Figure 3.2 shows the XRD profile of ZnGa$_2$O$_4$ nanoparticles synthesized by varying the volume ratio of Zn/Ga precursor solutions at a temperature of 200$^\circ$C for 3 h. It is observed that the FWHM of the (311) peak increases with the volume ratio of Zn/Ga precursors. When the volume ratio of Zn/Ga precursor solution is below 0.5, ZnO and Ga$_2$O$_3$ phases were detected by XRD, but no spinel ZnGa$_2$O$_4$ phase was found. Figure 3.3
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shows the XRD profile of ZnGa$_2$O$_4$ nanoparticles synthesized by varying the temperature and duration of growth by keeping the volume ratio of Zn/Ga precursor solutions as 2. The FWHM is found to be more or less same for hydrothermally grown samples for a duration of 3 h at 150°C and 200°C. The samples grown at 150°C for a growth time of 6 h resulted in bigger particles (15.5 nm) whereas at 200°C for 6 h, the size of the particle remains almost same as that grown at 3 h. The exact mechanism of growth is not well understood. In the present study we have chosen the optimum values of volume ratio of Zn/Ga precursors, temperature and time of hydrothermal growth as 2, 200°C and 3 h respectively. The average grain size (D) of the samples was estimated with the help of Scherrer equation [154] using the diffraction intensity of (311) peak.

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where, \(\lambda\) is the x-ray wavelength, \(\beta\) is the full width at half maximum (FWHM) of the ZnGa$_2$O$_4$ (311) line and \(\theta\) is the diffraction angle. The grain size of the nanoparticles is in the range 8-17 nm and lattice parameter calculated were found to vary with the growth conditions and is in quite agreement with reported values.

FT-IR spectra of the nanosized ZnGa$_2$O$_4$ powders are shown in the figure 3.4. The peaks at 3318 cm$^{-1}$ is due to the (O-H) vibration of H$_2$O absorbed by the sample. The peaks at about 584 cm$^{-1}$ and 409 cm$^{-1}$ represent the characteristic metal-oxygen (Zn-O and Ga-O) vibrations respectively. The sharp peak at 1382 cm$^{-1}$ corresponds to the adsorbed nitrate ions.
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Figure 3.4: FTIR spectra of the nanoparticles of ZnGa$_2$O$_4$ synthesized by hydrothermal method

Figure 3.5 shows the TGA profile of the as-prepared undoped ZnGa$_2$O$_4$ sample with a heating rate of 10$^\circ$C/min and a nitrogen flow rate of 100 ml/min. It is observed that the powder undergoes two phase transitions in different temperature regions. The first occurs below the temperature of 125$^\circ$C which could be attributed to the loss of water molecules associated with the particles. The weight loss between 125 and 550$^\circ$C is due to the removal of nitrates. The evaporation of the adsorbed moisture contributed to the major weight loss of 8%. The pyrolytic condensation of residual metal salts or hydroxides in air involved a weight loss less than 5%.
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Figure 3.5: TGA spectra of the ZnGa$_2$O$_4$ nanoparticle synthesized by hydrothermal method

The diffuse reflectance spectrum of the bulk and nanosized ZnGa$_2$O$_4$ powder in the visible region is shown in Figure 3.6. The diffuse reflectance spectroscopy measurements confirm the blue shift in the band gap of nanocrystals with respect to the bulk. The absorbance was calculated from the reflectance using Kubelka-Munk equation [168, 169]. Relative diffuse reflectance was measured with BaSO$_4$ powder as reference. The band gap 4.59 eV of nano ZnGa$_2$O$_4$ particles was estimated from the plot of $\{(k/s)h\nu\}^2$ versus $h\nu$, [109, 168, 169] which is shown in the figure 3.7, where $k$ and $s$ denote absorption and scattering coefficients, $h\nu$ the photon energy. The band gap of ZnGa$_2$O$_4$ nanoparticles is blue shifted from that of the bulk ZnGa$_2$O$_4$ (4.52 eV). This increase in the band gap is due to the quantum confinement effects.
**Figure 3.6:** Diffuse reflectance spectra of bulk and nanosized ZnGa$_2$O$_4$ powder

**Figure 3.7:** Plot of \([(k/s)h\nu]^2\) vs energy of (a) bulk and (b) nanosized ZnGa$_2$O$_4$ powder
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Figure 3.8: Room temperature photoluminescence emission spectra of bulk and ZnGa$_2$O$_4$ nanoparticles excited at $\lambda_{ex} = 254$ nm

Figure 3.8 shows the room temperature photoluminescence emission spectra of bulk and nano ZnGa$_2$O$_4$. The room temperature photoluminescence measurements of the nanocrystals monitored at an excitation wavelength of 254 nm gave a broad spectrum [185]. The diffuse reflectance spectra (Figure 3.6) indicates that gallium is responsible for the photoluminescence excitation of the prepared nanopowders of ZnGa$_2$O$_4$ [114]. However, the PL emission spectra shows some peaks at wavelengths of 399, 443, 453, 464, 470, 476, 484, and 493 nm when the nanophosphors were excited with the UV light of wavelength 254 nm. The excitation peak at
254 nm corresponds to the charge transfer from O\(^{2-}\) to Ga\(^{3+}\) at regular octahedral sites [196]. All the samples prepared at different volume ratio of Zn/Ga precursors exhibit broad emission spectra. These spectra exhibit certain peaks apart from the characteristic bell-shaped emission spectra of bulk ZnGa\(_2\)O\(_4\) phosphors as reported in literature [110, 114]. The isolated Ga\(^{3+}\) ion exhibits spectral lines at wavelengths of 438.07, 438.18, 486.30, and 499.38 nm in air [197]. Peaks observed in the emission spectra of the prepared ZnGa\(_2\)O\(_4\) nanophosphors may correspond to the electronic transitions of localized Ga\(^{3+}\) ion in the octahedral Ga-O sites which induces the electronic energy levels to split. The quantum effects in nanophosphors prepared in this study are predominant because it have much smaller particle size than those of the powder prepared by the conventional solid-state reaction. [185]. This leads to splitting of electronic energy levels of Ga\(^{3+}\) in the octahedral site of Ga-O resulting the peaks in the emission spectra. The blue emission band maximum at 470 nm corresponds to the self-activated luminescence of the host. The origin of the self activated blue emission around 437 nm in ZnGa\(_2\)O\(_4\) bulk is attributed to Ga\(^{3+}\) at octahedrally coordinated site [110, 114].

Figure 3.9(a) shows the TEM image of Eu doped ZnGa\(_2\)O\(_4\) prepared with 0.02 mol Eu\(_2\)O\(_3\) in the precursor solution. TEM image confirms the formation of nanoparticles of the spinel phosphor material. The average size of the spherically shaped particles was determined to be 8 nm. This result is consistent with what we had obtained from XRD analysis. Figure 3.9(b) shows the HRTEM images of the Eu doped ZnGa\(_2\)O\(_4\) nanoparticles. The d value 2.1 Å corresponds to the (400) planes of the ZnGa\(_2\)O\(_4\) nanoparticles. From the diffraction rings (Figure 3.9(c)) in the selected area electron diffraction (SAED) pattern, (220), (311), (400), (422), (511)
and (440) planes of ZnGa$_2$O$_4$ could be identified. The particle size distribution of the Eu doped ZnGa$_2$O$_4$ nanoparticles by counting the number of particles from the TEM image shown in figure 3.9(d) do assert the fact that most of the nanoparticles synthesized had the dimension 6-9 nm.

**Figure 3.9:** (a) TEM image (b) HRTEM image (c) SAED pattern and (d) particle size distribution from the TEM image of Eu doped ZnGa$_2$O$_4$ nanoparticles grown by hydrothermal method.
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Figure 3.10: Room temperature photoluminescence emission spectra of Eu doped ZnGa$_2$O$_4$ nanoparticles excited at $\lambda_{ex} = 397$ nm for different amount of Eu$_2$O$_3$ in the precursor solution.

From the ICP-AES results it is found that Eu/(Eu+Ga) is about 3.38%. Figure 3.10 shows the room temperature photoluminescent emission spectra of Eu doped ZnGa$_2$O$_4$ nanoparticles excited at 397 nm. The excitation energy almost coincides with the energy of $^7F_0 \rightarrow ^5L_6$ transitions of Eu$^{3+}$ ions, which is 3.147 eV [198]. Excitation at 397 nm yields the characteristic emissions of Eu$^{3+}$ corresponding to $^5D_j \rightarrow ^7F_j$ ($j=0, 1, 2, 3$ and $4$). The emission at 596 nm originates from the magnetic-dipole allowed $^5D_0 \rightarrow ^7F_1$ transition, indicating that Eu$^{3+}$ ions occupy a site with inversion symmetry. This is the only transition when Eu$^{3+}$ is situated at a site coinciding with a centre of symmetry. The emission at 619 nm corresponds
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To electric-dipole allowed $^5D_0 \rightarrow ^7F_2$ transition, which results in a large transition probability in the crystal field with inversion antisymmetry. The intensity of emission corresponds to the $^5D_0 \rightarrow ^7F_2$ transition is stronger than that of $^5D_0 \rightarrow ^7F_1$ transition. It is suggested that the Eu$^{3+}$ ions mainly occupy a site with inversion antisymmetry in the ZnGa$_2$O$_4$ host.

The emission at 701 nm is from $^5D_0 \rightarrow ^7F_4$ transition and at 653 nm is from $^5D_0 \rightarrow ^7F_3$ transition. The emission peaks at 583 nm corresponds to $^5D_0 \rightarrow ^7F_0$ transition. The observation of forbidden $^5D_0 \rightarrow ^7F_0$ transition indicates that some of the Eu ions are at low symmetry site. The detection of this transition suggests that Eu$^{3+}$ ions do not occupy a lattice site with inversion center. The emission at 543 nm is from $^5D_1 \rightarrow ^7F_1$ transition.

Figure 3.11: Variation of PL integral intensity of Eu doped ZnGa$_2$O$_4$ nanoparticles with amount of Eu$_2$O$_3$ in the hydrothermal precursor solution
The luminescent intensity of Eu doped ZnGa\textsubscript{2}O\textsubscript{4} nanoparticles increases with increase of the amount of Eu\textsubscript{2}O\textsubscript{3} in the precursor solution up to 0.01 mol and then it decreases which is shown in the figure 3.11. When the activator concentration increases above a certain level, luminescence begins to quench. Thus the emission intensity of \( ^5\text{D}_0 \rightarrow ^7\text{F}_j \) (\( j=0-4 \)) depends on the amount of Eu\textsubscript{2}O\textsubscript{3}. In this case, the pairing or aggregation of activator atoms at high concentration may change a fraction of the activators into quenchers and induce the quenching effect. The migration of excitation by resonant energy transfer between the Eu\textsuperscript{3+} activators can sometimes be so efficient that it may carry the energy to a distant killer or to a quenching centre existing at the surface of the crystal.

### 3.4 Conclusion

Undoped and Eu doped ZnGa\textsubscript{2}O\textsubscript{4} nanophosphors were synthesized by hydrothermal method by varying the process parameters such as temperature, time of growth, volume ratio of Zn/Ga precursor solutions and the amount of Eu\textsubscript{2}O\textsubscript{3} added to the precursor solution. The room temperature photoluminescence measurements of the nanocrystals monitored at an excitation wavelength of 254 nm gave a peak-shaped spectrum instead of the normally observed bell-shaped spectrum of bulk ZnGa\textsubscript{2}O\textsubscript{4}. The band gap of the ZnGa\textsubscript{2}O\textsubscript{4} nanoparticles is blue shifted compared with the bulk material due to quantum confinement effects. XRD and SAED results show Eu doped ZnGa\textsubscript{2}O\textsubscript{4} nanoparticles have spinel structure and the particle size 8 nm as confined by the TEM. Incorporation of Eu in the nanoparticles was confirmed by the ICP-AES studies. The red PL emissions from the intra-4f transition of Eu\textsuperscript{3+} ions are observed in Eu doped ZnGa\textsubscript{2}O\textsubscript{4} nanophosphors.
under an excitation of 397 nm. Luminescence quenching is observed in these nanophosphors as the amount of Eu$_2$O$_3$ increases. These nanophosphors can be used as a blue to red converter for solid state lighting applications.
Undoped and Eu doped ZnGa$_2$O$_4$ nanoparticles