CHAPTER 3

Synthesis and Characterization of Oxide Phosphors
This chapter is divided into two parts. Part A deals with synthesis and characterization of bulk Zn$_2$GeO$_4$:Mn$^{2+}$ phosphor and the effect of Mg addition on structural and optical properties are discussed. On the basis of analysis the presence of a sub-band gap is observed and possible mechanism of luminescence in the phosphor is identified.

Part B discusses about synthesis and characterization of bulk Mg$_2$GeO$_4$:Mn phosphor and the effect of Zn codoping on structural and optical properties. Zn codoping is found to increase photoluminescent (PL) emission intensity.
PART A

Synthesis and characterization of $\text{Zn}_2\text{GeO}_4: \text{Mn}^{2+}$ phosphor
3A.1. Introduction

Thin film electroluminescent devices are mostly based on sulphide phosphors (ZnS, SrS etc) [1-4]. Recently, oxide phosphors [5, 6] are considered as potential substitutes owing to their extreme stability in vacuum, moisture insensitivity and non-degradation under electron bombardment. Several oxide phosphor hosts like ZnGa$_2$O$_4$, Zn$_2$GeO$_4$, Zn$_2$SiO$_4$, Y$_2$O$_3$ etc have been extensively studied [7-13]. Among them, Zn$_2$GeO$_4$ doped with Mn is an excellent green emitting phosphor. Rhombohedral Zn$_2$GeO$_4$ is similar to Zn$_2$SiO$_4$, but have lower crystallization temperature. Thin films of Zn$_2$GeO$_4$:Mn$^{2+}$ grown using RF magnetron sputtering and pulsed laser deposition techniques also show good luminescent characteristics [13-15]. The green emission in Zn$_2$GeO$_4$:Mn$^{2+}$ is due to the transitions in 3d$^5$ electrons of Mn$^{2+}$ that substitute tetrahedral Zn$^{2+}$ sites [13]. Several methods can be adopted to enhance the luminescent properties of these phosphors. Co-doping is one such efficient approach. In Zn$_2$GeO$_4$, co-dopants that substitute Ge$^{4+}$ and Zn$^{2+}$ can provide positive results. Among the various ions (Mg$^{2+}$, Cd$^{2+}$, Ba$^{2+}$ etc.) that can replace Zn$^{2+}$ in Zn$_2$GeO$_4$, Mg$^{2+}$ is a better choice since its ionic radius is more comparable with Zn$^{2+}$ than other ions. In the present work, the effect of Mg$^{2+}$ incorporation on structural and luminescent properties of Zn$_2$GeO$_4$:Mn is studied in detail.

3A.2. Experiment

The samples were prepared by conventional high temperature solid-state reaction of constituent oxides namely ZnO (Alfa Aesar 99.99%), MgO (Alfa Aesar 99.99%) GeO$_2$. (Alfa Aesar 99.999%) Manganese was added in the form of manganous acetate [Mn(CH$_3$COO)$_2$]. The powders were mixed
stoichiometrically in ethanol medium and calcined in air at 1200°C for 12 hrs in a tube furnace to obtain Zn$_{1.96-1.96x}$Mg$_{1.96x}$GeO$_4$:Mn$_{0.04}$ (x was varied from 0 to 0.5). All samples were doped with 2 at.% of Mn which was the optimized concentration of Mn in Zn$_{2-2x}$GeO$_4$:Mn$_{2x}$ phosphor which has maximum PL emission intensity. The relative luminescence quantum efficiency (QE) of phosphor was measured using a standard lamp phosphor, BaMgAl$_{10}$O$_{17}$ (BAM), of known quantum efficiency (90%). For the calculations, integrated PL intensity of BAM and phosphors were measured at identical conditions such as sample weight, instrument settings, temperature (RT) and excitation wavelength (300nm).

The quantum efficiency of unknown sample is calculated using the equation,

$$QE_{(Sample)} = \frac{QE_{BAM} \times \int I_{Sample}}{\int I_{BAM}}$$ (3.1)

Where, \(\int I_{Sample}\) and \(\int I_{BAM}\) are the integrated emission intensities of the unknown sample and the BAM phosphor, respectively.

3A.3. Results and Discussion

The optimum concentration of Mn for which maximum luminescent intensity observed was found by preparing 3 samples with 1 at. %, 2 at. % and 3 at. % Mn doped Zn$_2$GeO$_4$. The PL emission spectrum of the bulk phosphors is shown in figure 3.1. From the figure it is clear that the sample with 2 at. % doped Mn showed maximum luminescent intensity. The emission wavelength was same for all the three samples. The reduction in luminescent intensity above
2 at.% Mn doped sample can be attributed to luminescent quenching due to increased concentration of the activator which is often observed in phosphors.

![Figure 3.1 PL emission spectra of Zn2GeO4:Mn phosphor at various Mn concentrations](image)

Figure 3.1 PL emission spectra of Zn2GeO4:Mn phosphor at various Mn concentrations ($\lambda_{\text{exc}} = 332$ nm)

### 3A.3.1 X-ray diffraction studies

Figure 3.2 shows the XRD patterns of $\text{Zn}_{1.96-1.96x}\text{Mg}_{1.96x}\text{GeO}_4:\text{Mn}_{0.04}$ ($0 \leq x \leq 0.5$). The standard spectrum of undoped Zn$_2$GeO$_4$ is plotted for reference [14]. The XRD pattern clearly implies that Mg is randomly substituting Zn in Zn$_{1.96}\text{GeO}_4:\text{Mn}_{0.04}$ for concentrations up to $x = 0.25$ forming a single phase,
preserving the hexagonal symmetry of the host lattice. No traces of constituent oxides were found in the diffraction patterns. The peaks other than that of $Zn_2GeO_4$ are identified to be of orthorhombic $Mg_2GeO_4$ [15]. But above $x = 0.25$, phase segregation commences limiting the solid solubility of Mg in $Zn_{1.96}GeO_4: Mn_{0.04}$. In wurtzite $Zn_{1.96}Mg_xO$, Mg is found to be soluble up to $x = 0.33$ [16-18]. As the crystal structures of $Zn_2GeO_4$ (rhombohedral) and $Mg_2GeO_4$ (orthorhombic) are different, substitution of Zn with Mg will not occur for all concentrations and results in phase separation. Alloying is observed up to $x = 0.25$ and the lattice constants of $Zn_{1.96-1.96x}Mg_{1.96x}GeO_4:Mn_{0.04}$ are expected to change as $Zn^{2+}$ and $Mg^{2+}$ have different ionic radii (0.60pm and 0.57pm respectively) for four coordination [19].

![Figure 3.2 XRD patterns of $Zn_{1.96-1.96x}Mg_{1.96x}GeO_4:Mn_{0.04}$, $0 \leq x \leq 0.5$. * represents peaks of $Mg_2GeO_4$](image-url)
The c-axis length and cell volume was calculated from the observed XRD data [20], the variation of which with Mg concentration is shown in figures 3.3 and 3.4 respectively. The c-axis length of Zn$_2$GeO$_4$ is 9.53 Å and that of Mg$_2$GeO$_4$ is 4.91 Å. The c-axis length show a contraction with increased Mg substitution up to $x = 0.25$. But for $x = 0.30$, 0.35 and 0.5, c-axis length increases. This is because as Mg concentration increases, simple substitution of Mg terminates and starts to segregate into different phases. However cell volume increases continuously up to $x = 0.25$ and decreases for $x = 0.30$, 0.35 and 0.5 which is due to an elongation in the ‘$a$’ parameter up to $x = 0.25$. The difference in cell volume is assumed to be due to the difference in ionic radii of Zn$^{2+}$ and Mg$^{2+}$ which also gives rise to difference in c-axis length.
The variation of FWHM of (410) XRD peak with Mg concentration is plotted in figure 3.5. There is gradual variation in the FWHM value up to $x = 0.25$ which indicates Mg alloying in the $\text{Zn}_2\text{GeO}_4$ lattice. However it shows a sudden increase at $x = 0.30$ and 0.35 for which phase segregation takes place and for $x = 0.5$ it again decreases. The substitution of Mg at Zn sites is expected to broaden XRD peak and interestingly maximum broadening is observed for $x = 0.35$ at which phase segregates.

The $c$-axis length, cell volume and FWHM show almost similar behaviour with Mg substitution. A sudden change at $x = 0.30$ and 0.35 is observed for all parameters which is due to the in-built strain caused by Mg substitution in the lattice and due to this strain phase segregates and above $x = 0.35$ $\text{Zn}_2\text{GeO}_4$ and $\text{Mg}_2\text{GeO}_4$ is separately formed and therefore beyond $x = 0.35$ these parameters randomly approaches its previous value for which solid solution exists.
Therefore it can be concluded from the XRD studies that phase segregation occurs due to the inbuilt strain in the lattice due to Mg substitution and Mg is replacing Zn substitutionally.

3A.3.2 Optical characterization

(a) Diffused reflectance spectra analysis

Figure 3.6(a) shows the DRS spectra of Zn$_{1.96-1.96x}$GeO$_4$:Mn$_{0.04}$ for the various Mg concentrations and the variation of band gap with Mg concentration. As the Mg doping percentage increases, the absorption edge blue-shifts.
Figure 3.6 (a) The DRS spectra of $\text{Zn}_{1.96}$-$\text{GeO}_4$:Mn$^{0.04}$, Mg (arrow indicates x variation from 0 to 0.5 in steps of 0.05, final one being $x = 0.5$) (b) Band gap of pure $\text{Zn}_2\text{GeO}_4$ and $\text{Zn}_{1.96}\text{GeO}_4$:Mn$^{0.04}$. Inset shows the variation in band gap with Mg concentration.
The band gap of pure Zn$_2$GeO$_4$, Zn$_{1.96}$GeO$_4$:Mn$_{0.04}$ and Zn$_{1.96-}$Mg$_{1.96}$GeO$_4$:Mn$_{0.04}$ samples were calculated from the $((k/s)_h/\nu)^2$ vs $\nu$ plots, where k and s denotes the absorption and scattering coefficients respectively. The band gap of pure Zn$_2$GeO$_4$ is found to be 4.57 eV and that of Mn doped Zn$_2$GeO$_4$ is 3.44 eV (fig 3.6(b)). The reduced band gap for Zn$_{1.96}$GeO$_4$:Mn$_{0.04}$ sample is due to the formation of a sub-band gap states (discussed later). In the normal case Mg$^{2+}$ replaces Zn$^{2+}$ in Zn$_{1.96}$GeO$_4$:Mn$_{0.04}$ and there is a limit to this simple substitution since Zn$_2$GeO$_4$ (rhombohedral) and Mg$_2$GeO$_4$ (orthorhombic) crystallizes in to different crystal structures. Therefore the substitution of Mg$^{2+}$ at Zn$^{2+}$ sites creates strain in the lattice due to the reduced size of Mg$^{2+}$ which results in the blue shift of the absorption edge.

(b) Photoluminescence studies

Figure 3.7 shows PL emission spectra of Zn$_{1.96-1.96}$Mg$_{1.96}$GeO$_4$:Mn$_{0.04}$(0 $\leq x \leq 0.5$). PL emission intensity is higher for $x = 0.05$, 0.10, 0.15, 0.20 when compared to $x = 0$ sample and intensity lowers beyond $x = 0.25$ compared to the undoped sample, the maximum being observed for the sample doped with 5 at. % Mg ($x = 0.05$).

The green luminescence at 535nm is observed from $^4T_1 \rightarrow ^6A_1$ transitions of 3d$^5$ electrons of Mn$^{2+}$ which substitutes the tetrahedrally coordinated Zn$^{2+}$ ions in rhombohedral Zn$_2$GeO$_4$, as the host provides only tetrahedral sites for substitution [14]. When Mg is co-doped in Zn$_{1.96}$GeO$_4$:Mn$_{0.04}$, luminescent intensity varies due to the change in effective crystal field of tetrahedrally coordinated Mn$^{2+}$ ions. When Mg$^{2+}$ is incorporated in the lattice it creates excited state energy levels (consisting of 3s and 3p) near the excited state of Mn$^{2+}$ (comprising of $^4T_1(^4G)$, $^4T_2(^4G)$, $^4A_1(^4G)$, $^4T_1(^4P)$, shown in fig 3.10). Therefore
transition from the Mg levels to ground state of Mn\(^{2+}\) becomes more permissible, since the transition is more spin allowed compared to 3d\(^5\) transitions of Mn\(^{2+}\) [21].

![Graph showing PL emission spectra of Zn\(_{1.96-1.96x}\)Mg\(_{1.96x}\)GeO\(_4\):Mn\(_{0.04}\) (0 \(\leq x \leq 0.5\))](image)

Figure 3.7 PL emission spectra of Zn\(_{1.96-1.96x}\)Mg\(_{1.96x}\)GeO\(_4\):Mn\(_{0.04}\) (0 \(\leq x \leq 0.5\)), \(\lambda_{\text{exc}} = 300\text{nm}\)

However when concentration of Mg is increased, luminescent intensity decreases because effective transfer of charge via excited states of Mg will not take place due to inbuilt strain in the lattice. The quantum efficiency of the phosphor \((\text{Zn}_{1.862}\text{Mg}_{0.098}\text{GeO}_4:\text{Mn}_{0.04})\) that showed maximum luminescent intensity is 41\%, relative to BAM phosphor.

Figure 3.8 shows excitation and emission spectra of undoped Zn\(_2\)GeO\(_4\). Undoped Zn\(_2\)GeO\(_4\) shows absorption at 266nm with a shoulder at 251nm for emission at 507nm. Pure Zn\(_2\)GeO\(_4\) shows a broad emission from 300 to 650
peaking at 507nm when excited with 266nm. But when Mn\(^{2+}\) is added the emission becomes narrow and shifts to 535nm and excitation maximum shifts to 335nm in addition to 266 nm (band edge) and 285 nm (direct excitation of Mn\(^{2+}\)) absorption indicating the presence of a sub-band gap. The green luminescence from the undoped sample is a signature of intrinsic defect levels in the lattice during its synthesis.

![Fig 3.8](image.png)

Figure 3.8 PLE spectra of Pure Zn\(_2\)GeO\(_4\) monitored at 507nm. Inset shows the emission spectra when excited at 266nm

Figure 3.9 shows PL excitation spectra of Zn\(_{1.96}\)GeO\(_4\):Mn\(_{0.04}\) and inset shows variation of PLE peak wavelength with respect to the Mg addition in Zn\(_{1.96}\)GeO\(_4\):Mn\(_{0.04}\). PLE shifts to lower wavelength as Mg concentration is increased which is consistent with the results obtained from DRS spectra. The
spectra shows a shoulder at 285nm, while peak wavelength is at 335nm for x = 0 sample. The shoulder at 285nm and peak at 425nm is evidently direct excitation of tetrahedrally coordinated Mn$^{2+}$ ions [22].

![Graph showing PLE spectra of Zn$_{1.96}$GeO$_4$:$Mn_{0.04}$, inset shows variation of PL excitation with Mg concentration in Zn$_{1.96-x}$Mg$_x$GeO$_4$:$Mn_{0.04}$](image)

Figure 3.9 PLE spectra of Zn$_{1.96}$GeO$_4$:$Mn_{0.04}$. Inset shows variation of PL excitation with Mg concentration in Zn$_{1.96-x}$Mg$_x$GeO$_4$:$Mn_{0.04}$

The bottom of the conduction band of Zn$_2$GeO$_4$ is comprised of Ge 4p orbitals with a small contribution from Zn 4s and 4p orbitals and the upper part of the valence band is composed of O 2p levels [23]. The mechanism for the emission at 535nm is identified as band to band absorption and non-radiative transfer to a center, from which resonant transfer to activator takes place. This center lies nearly 1eV below the conduction band and is likely to be an oxygen defect which is also observed in the DRS spectra (fig 3.6). This can be formed
via migration of octahedrally coordinated Ge\(^{4+}\) ions to tetrahedral position forming Ge\(^{3+}\) ions [24]. Since the vapour pressure of Zn is high and high temperature solid state reaction is employed for the phosphor synthesis, Zn evaporation will take place leaving behind a vacancy and thereby occupying Zn vacancy sites by Ge\(^{3+}\) ions migrated from the octahedral sites. This is also confirmed from EDX data. In all the samples, the cation ratio (Zn/Ge) ratio was found to be less (1.3 for x = 0) than the actual value (1.96 for x= 0). In ZnO, a donor level 0.8eV below the conduction band is observed which gives rise to green luminescence and is created due to oxygen vacancy [25]. When Mn is added to the Zn\(_2\)GeO\(_4\) host, it creates excited state energy levels near this center in such a manner that the charge transfer to Mn will take place through absorption via this center along with band to band absorption (266nm). Another possibility is Zn vacancy which could form an acceptor level above the valence band. This is also observed in ZnO, where an acceptor level nearly 0.8eV above valence band is formed due to Zn vacancy [25]. But resonant transfer from a low lying level to excited state levels of Mn\(^{2+}\) is not possible. Other possibility is defect generated due to germanium. But that defect level will not be perturbed by adding Mg replacing Zn into tetrahedral position. Since the ionic radii of Mg\(^{2+}\) and Ge\(^{4+}\) is not comparable hardly a chance exists for Mg to replace Ge in Zn\(_2\)GeO\(_4\). Therefore this trap level could be due to oxygen deficiency. The energy levels and the mechanism of PL emission in Zn\(_2\)GeO\(_4\): Mn is schematically represented in figure 3.10.

When Mg is added to the system, it creates energy levels near the excited state levels of Mn\(^{2+}\) and also it perturbs the V\(_O\) level thereby shifting the
absorption edge. Therefore the DRS spectra and PLE spectra shows a blue shift when Mg is alloyed to Zn$_2$GeO$_4$:Mn host matrix.

Figure 3.10 Energy level scheme describing the excitation and emission mechanism of Zn$_2$GeO$_4$:Mn$^{2+}$ phosphor

3A.3.3 Electron Spin resonance (ESR) studies

The electron paramagnetic/spin resonance is a well-known technique for investigations of defects in crystalline and non-crystalline materials. The parameters resulting from the analysis of the observed spectra can provide the local site symmetry around the paramagnetic centers and the structure of the host material. Besides, ESR permits a chemical identification of the investigated center and frequently permits identification of associated defects along with a determination of their charge states and an estimate of their concentrations [26]. Figure 3.11 shows ESR spectra of Zn$_{1.96-1.96x}$Mg$_{1.96x}$GeO$_4$:Mn$_{0.04}$ for 0 ≤ x ≤ 0.5.

The spectra shows a strong and broad signal in the range of 3000 - 4000 gauss and can be assigned to V$_o$ (g ≈ 2.0), which was also observed in other hosts [2,16]. Also in the lower magnetic field range (850-2000 G) a broad peak with six hyper fine lines is observed.
In ZnS:Mn it is observed that at lower Mn concentration, the six line hyperfine structure of the fine structure transition $11/2 >$ to $-1/2 >$ of Mn$^{2+}$ ion will appear in the spectra while at higher concentrations, due to clustering, it will form a broad single spectrum [26]. The hyperfine structure originates from the interaction between $^{55}$Mn nucleus of spin $I = 5/2$ and the electron cloud.

![ESR spectra](image)

**Figure 3.11** ESR spectra of Zn$_{1.96-1.96-x}$Mg$_{1.96-x}$GeO$_4$·Mn$_{0.04}$ for $0 \leq x \leq 0.5$. Inset shows enlarged view of the spectra in lower magnetic fields.

More over crystal field has much influence on the nature of spectra. It was reported that the EPR signals of the ions with unpaired electrons may shift to low magnetic field (g value increases) at the site with stronger crystal field [27, 28]. Here also we get a signal with six hyperfine lines in the low magnetic
field regime (inset of figure 3.11). Three different sites of Eu\textsuperscript{2+} were proposed in Ba\textsubscript{3}MgSi\textsubscript{2}O\textsubscript{8}:Eu, Mn phosphor as they observed signals at three different magnetic field regimes [27]. But here Mn\textsuperscript{2+} is supposed to replace Zn\textsuperscript{2+} as there is charge imbalance and variation in ionic radii with Ge\textsuperscript{3+} ions. Besides, if at high temperature, Mn\textsuperscript{2+} has been oxidized to Mn\textsuperscript{4+} and replaced Ge\textsuperscript{3+} (which is possible due to similar ionic radii for both ions in six coordination), the luminance would be in the red region. But no red luminescence could be observed in the PL spectra. So the possibility of Mn\textsuperscript{2+} and Mn\textsuperscript{4+} replacing Ge\textsuperscript{4+} ion is ruled out.

The deviation from \( g_e \) can also be from the contribution of orbital magnetic moment and can be written as

\[
g - g_e = \frac{\xi}{E_{d1} - E_{d2}}
\]

where \( \xi \) is the spin-orbit coupling constant and \( E_{d1} \) and \( E_{d2} \) represents energy gap between d orbitals [29]. In some cases, the contribution of the orbital magnetic moments is mixed into the \( g \) value, which is related to the energy gap between the ground state and the lowest excitation state. The narrower the gap is, the more orbital magnetic moment is contributed, which results in larger \( g \) value.

The peak around 3300 G (\( g \approx 2 \)) can be attributed to singly ionized oxygen vacancy (\( V_0 \)). This peak due to singly ionized oxygen vacancy (\( V_0 \)) is also observed in undoped pure Zn\textsubscript{2}GeO\textsubscript{4} due to its native defects [30]. In ZnS:Mn the broadening of resonant signal (highly resolved six lines) is observed and it is attributed to the clustered Mn ions due to higher concentration which strongly influence one another through their magnetic moments [26]. So the corresponding broadening is also observed in the spectra. However a strong signal at \( g \approx 2 \) due to singly ionized Zn\textsuperscript{+} vacancy is observed by Tian \textit{et al.} in
zeolite [31]. But hardly a chance exists for possibility of existence of Zn\(^+\) ion in the lattice as it is highly unstable. As Mg is incorporated in to the Zn\(_2\)GeO\(_4\) system, a variation in the ESR spectra is observed which is expected as now system is getting too complicated and above \(x = 0.25\) no solid solution exists and phase segregates.

**Conclusion**

In summary, Mg alloyed Zn\(_{1.96}\)GeO\(_4\):Mn\(_{0.04}\) phosphor was prepared by solid state reaction. The structural analysis reveals the formation of solid solution up to \(x = 0.25\) in Zn\(_{1.96-1.96x}\)Mg\(_x\)GeO\(_4\):Mn\(_{0.04}\). Beyond \(x = 0.25\), phase segregation occurs. The absorption edge as observed from DRS and PLE spectra of Mn and Mg doped samples indicates the presence of a sub-band gap and was found to be blue shifted with increase in Mg substitution. The PL emission spectra exhibits increase in luminescent intensity with Mg concentration at \(x = 0.05\) in Zn\(_{1.96-1.96x}\)Mg\(_{1.96x}\)GeO\(_4\):Mn\(_{0.04}\) phosphor. The phosphor can be used as an active layer in ACTFEL devices.
PART B

Synthesis and characterization of Mg$_2$GeO$_4$: Mn$^{2+}$ phosphor
3B.1 Introduction

One of the necessary criteria to be a phosphor host is the wide band gap. The band gap should be greater than 3eV so that visible radiation emitted by the activator/impurity is not absorbed by the host. But there is a limit to band gap for electroluminescent display phosphors, above which no electroluminescence is observed, since in most cases luminescence arises due to resonant energy transfer from the host to activator. Efficient host materials for ACTFEL phosphors are generally limited to those materials with bandgap energies in the range of 3.5-4.5 eV. Manganese is an excellent activator for yellow (in ZnS) [2], green (ZnGa2O4, Zn2GeO4) and red (ZnMgS) [32], Mg2GeO4 [33]) emissions. Eu and Cr doped Mg2GeO4 also shows red emission, serves as a phosphor for plasma display panels [32, 33]. In orthorhombic Mg2GeO4 (a = 10.29 Å, b = 6.023 Å, c = 4.905 Å) Mg2+ ions occupy tetrahedral sites while Ge3+ ions occupy octahedral sites in crystal lattice. The wide optical band gap of Mg2GeO4 makes it as a suitable candidate for wide band gap oxide phosphor. However efficient high field electroluminescence from Mg2GeO4 host material is not observed due to its high band gap and inefficient transfer of energy from the host to activator. Also Mg2GeO4: Mn phosphor has not been widely studied for luminescent applications. Co-doping has been proved as an excellent technique for engineering the band gap [17, 21, 36]. Among the various ions that can replace Mg, Zn is better choice due to its similarity in ionic radii and valency. More over the band gap of ZnO has been engineered by alloying it with Mg for many optoelectronic applications [17]. Alloying up to x = 0.33 is observed in Zn1-xMgxC thin films [36]. Due to abundance and non-toxicity, compared to other ions like Cd, Zn is more appropriate co-dopant for
engineering the band gap of Mg\textsubscript{2}GeO\textsubscript{4}. In the present work, the effect of zinc alloying on the crystal structure, band gap and photoluminescence of Mg\textsubscript{2}GeO\textsubscript{4}:Mn is studied.

### 3B.2 Experiment

The samples were synthesised by conventional high temperature solid-state reaction of constituent oxides namely MgO, ZnO, GeO\textsubscript{2}. Manganese was added in the form of manganous acetate [Mn(CH\textsubscript{3}COO)\textsubscript{2}]\textsuperscript{2+}. The stoichiometric powders were mixed in ethanol medium and calcined in air at 1200\textdegree{}C for 12 hrs in a tubular furnace to obtain Mg\textsubscript{1.96-1.96x}Zn\textsubscript{1.96x}GeO\textsubscript{4}:Mn\textsubscript{0.04} (x was varied from 0 to 0.5). The concentration of Mn was fixed at 2 at. \% in all the samples. The concentration of Zn was varied from 0 to 50 at.\% of Mg.

### 3B.3 Results and Discussion

#### 3B.3.1 X-ray diffraction studies

Figure 3.12 shows XRD patterns of pure Mg\textsubscript{2}GeO\textsubscript{4}:Mn, pure Zn\textsubscript{2}GeO\textsubscript{4}:Mn and Mg\textsubscript{1.96-1.96x}Zn\textsubscript{1.96x}GeO\textsubscript{4}:Mn\textsubscript{0.04} at different concentrations (x = 0.1, 0.15, 0.20, 0.25, 0.5) of zinc. The pattern clearly shows the formation of solid solution up to x = 0.10. But above x = 0.10, additional peaks are observed indicating phase segregation. These additional peaks are identified as that of Zn\textsubscript{2}GeO\textsubscript{4}. No traces of constituent oxides like ZnO and MgO, were found in the XRD pattern as the pattern matches well with the JCPDS data of Zn\textsubscript{2}GeO\textsubscript{4} [14] and Mg\textsubscript{2}GeO\textsubscript{4} [15]. Normally magnesium germenate crystallizes in orthorhombic structure and zinc germenate crystallizes in rhombohedral structure, thereby limiting simple incorporation of Zn in to Mg\textsubscript{2}GeO\textsubscript{4} lattice. Also the ionic radii of Zn and Mg differ; substituting Mg with Zn will not be...
possible for all concentrations and at a particular concentration phase will start to segregate. The phase segregation occurs due to inbuilt strain due to the difference in ionic radii and strain reaches a maximum at particular Zn concentration. However in $\text{Zn}_{1.96-1.96x}\text{Mg}_{1.96x}\text{GeO}_4$ Mg forms solid solution up to $x=0.3$ clearly indicating that rhombohedral $\text{Zn}_2\text{GeO}_4$ have more stability than $\text{Mg}_2\text{GeO}_4$ naturally favouring the formation of $\text{Zn}_2\text{GeO}_4$.

Figure 3.12 XRD patterns of $\text{Mg}_{1.96-1.96x}\text{Zn}_{1.96x}\text{GeO}_4: \text{Mn}_0.04$ ($0 \leq x \leq 1$) JCPDS of $\text{Mg}_2\text{GeO}_4$ is shown as reference.

Therefore as more and more Zn adds to the $\text{Mg}_2\text{GeO}_4: \text{Mn}$ system, formation of $\text{Zn}_2\text{GeO}_4: \text{Mn}$ is favoured and when $x=0.5$, $\text{Zn}_2\text{GeO}_4$ phase got enhanced thereby forming $\text{Zn}_{1.96-1.96x}\text{Mg}_{1.96x}\text{GeO}_4: \text{Mn}$. The cell volume [20] is
found to increase with x which is expected as the cell volume of Zn$_2$GeO$_4$ is larger than that of Mg$_2$GeO$_4$ (fig. 3.13).

![Graph showing cell volume and band gap variation with Zn concentration.](image)

Figure 3.13 Variation of Cell volume and band gap with Zn concentration. Straight (dashed) line shows apparent linear fit to data.

The band gap of Mg$_2$GeO$_4$:Mn$^{2+}$ and Zn$_2$GeO$_4$:Mn$^{2+}$, calculated from the spectra are 5 eV and 3.45 eV respectively. In both cases strong sub-band absorption is observed. This sub band state lie nearly 1 eV below the conduction band is formed due to intrinsic oxygen vacancies during the compound formation. The schematic energy level scheme is shown in the figure 3.14.

3B.3.2 Diffused reflectance spectra (DRS) analysis

The variation of band gap of Mg$_2$GeO$_4$:Mn with Zn concentration (x) is shown in figure 3.15. As x increases band gap is found to be red-shifted. Figure clearly indicates mixed phase for doped samples (x = 0.15, 0.2, 0.25 and 0.5).
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Figure 3.14 Energy level scheme describing the excitation and emission mechanism of $\text{Mg}_2\text{GeO}_4:\text{Mn}$ phosphor

Figure 3.15 The band gap of $\text{Mg}_{1.96-1.96x}\text{Zn}_{1.96x}\text{GeO}_4:\text{Mn}_{0.04+x}$, $0 \leq x \leq 0.5$
So from the DRS spectra it is concluded that formation of solid solution is favoured for the zinc addition up to \( x = 0.10 \) and beyond that phase segregation occurs due to inbuilt strain in the lattice. The shift in band gap can be attributed to difference in ionic radii of \( \text{Zn}^{2+} \) and \( \text{Mg}^{2+} \) ions. Moreover when Zn is co-addition in to \( \text{Mg}_2\text{GeO}_4 \) system, \( \text{Zn}^{2+} \) will create states below the sub band levels created due to oxygen vacancy. So as more and more Zn gets added in to the \( \text{Mg}_2\text{GeO}_4 \) matrix, the band gap reduces.

### 3B.3.3 Photoluminescence studies

Figure 3.16 shows PL emission spectra of \( \text{Mg}_{1.96-1.96x}\text{Zn}_{1.96x}\text{GeO}_4:\text{Mn}_{0.04} \) \((0 \leq x \leq 0.25)\) samples.

![Photoluminescence spectra graph](image)

Figure 3.16 PL emission spectra (red) of \( \text{Mg}_{1.96-1.96x}\text{Zn}_{1.96x}\text{GeO}_4 \) \((0 \leq x \leq 0.25), \lambda_{\text{exc}} = 300 \text{ nm}\)
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All samples show emission in the red region and has intensity greater than Zn free sample. But the peak emission wavelength changes as x varies. In Mg$_2$GeO$_4$:Mn the emission is observed from tetrahedrally coordinated Mn$^{2+}$ at Mg sites [33]. The 3d$^5$ electrons of Mn$^{2+}$ is highly influenced by crystal field environment. The crystal field environment determines the colour or the emission wavelength of the activator. Moreover the energy transfer mechanism is not so efficient as in the case of Zn$_2$GeO$_4$:Mn. In Zn$_2$GeO$_4$ the mechanism of PL is identified as resonant energy transfer from a sub-band gap level, due to intrinsic defects, to Mn$^{2+}$ levels [24]. In Mg$_2$GeO$_4$ also a sub-band gap level is observed as the Mn$^{2+}$ emission is triggered from a level which is nearly 1 eV below the conduction band. But this level is not in the vicinity of excited levels of Mn$^{2+}$ for efficient resonant energy transfer to take place. But as more Zn is added to the system, transfer will take place to Mn$^{2+}$ levels through Zn$^{2+}$ levels formed near Mn$^{2+}$ levels. This is also observed in DRS measurements as reduction in band gap is observed as more Zn adds to the system.

However no red emission can be detected from x = 0.5 sample indicating the complete replacement of Mn$^{2+}$ at Zn$^{2+}$ sites in Zn$_2$GeO$_4$. Therefore similar to the formation of Zn$_2$GeO$_4$, which is more favourable, Mn$^{2+}$ is more likely to replace Zn$^{2+}$ rather than Mg$^{2+}$. Green emission (fig 3.17) is also detected from the samples at and above x = 0.15 clearly showing the limit of solid solubility of Zn in Mg$_2$GeO$_4$:Mn. But in Zn$_2$GeO$_4$:Mn$^{2+}$, Mg is found to be soluble up to x = 0.3. This is due to greater stability of rhombohedral Zn$_2$GeO$_4$ structure compared to orthorhombic Mg$_2$GeO$_4$. The green emission at 535 nm can be attributed to $^4T_1 \rightarrow ^6A_1$ transition of Mn$^{2+}$ in Zn$_2$GeO$_4$ and gets enhanced when Zn concentration increases. The photoluminescence excitation (PLE)
spectra for red emission (653nm) are shown in the figure 3.18. A broad excitation peaking at 268 nm is obtained for Mg$_2$GeO$_4$:Mn which is found to be red-shifted as more Zn$^{2+}$ replaces Mg$^{2+}$.

(a) $x = 0.15$
(b) $x = 0.20$
(c) $x = 0.25$
(d) $x = 0.50$
(e) $x = 1.00$

![Figure 3.17 Room temperature Photoluminescent emission spectra (green) of Mg$_{1.96-x}$GeO$_4$:Mn$_{0.04}$ ($0 \leq x \leq 0.5$), $\lambda_{\text{exc}} = 300$ nm](image)

In Zn$_2$GeO$_4$:Mn PLE at 332 nm is obtained for emission at 535nm showing the formation of sub-band gap. Since increased Zn concentration results in phase segregation, the excitation for red emission shifts to higher wavelength region indicating the presence of Zn$_2$GeO$_4$. The PLE spectra for $\lambda_{\text{em}} = 535$ nm, show a peak at 300nm, for $x = 0.50$ sample, indicating the formation of Zn$_{1.96-x}$Mg$_{1.96x}$GeO$_4$, Mg being substituted for Zn, there by emphasizing the fact that formation of Zn$_2$GeO$_4$ is more favored rather than Mg$_2$GeO$_4$. 138
3B.3.4 Electron spin resonance (ESR) studies

Figure 3.19 shows the variation ESR spectra for various concentrations of Zn in Mg$_2$GeO$_4$:Mn phosphor. It is clear from the spectra (see figure 3.20) that both hosts offer entirely different crystal field to the Mn$^{2+}$ ions or we can say that the environment as observed by Mn$^{2+}$ in both cases is entirely different. But as more Zn adds to Mg$_2$GeO$_4$:Mn system, the spectra shows variation and at $x = 0.25$ the spectrum is almost similar to Zn$_2$GeO$_4$:Mn thereby emphasizing the fact that the formation of Zn$_2$GeO$_4$ is more favoured. For $x = 0$ a strong signal at $g = 2$ is observed which can be attributed to singly ionized oxygen vacancy and also small isolated signals related to Mn is also observed.
Figure 3.19 ESR spectra of $\text{Mg}_{1.96-1.96x}\text{Zn}_{1.96x}\text{GeO}_4:\text{Mn}_{0.04}$ for $0 \leq x \leq 0.25$

Figure 3.20 ESR spectra of $\text{Zn}_2\text{GeO}_4:$Mn and $\text{Mg}_2\text{GeO}_4:$Mn
Synthesis and characterization of Mg$_2$GeO$_4$:Mn$^{2+}$ phosphor

Conclusion

Manganese doped Mg$_2$GeO$_4$ is synthesized by solid state reaction. The phosphor shows emission in red region. The effect of Zn alloying on structural and optical properties have been explored in detail. XRD patterns show solid solution formation up to 10 at% Zn addition and beyond that phase segregation occurs. When Zn is added in to Mg$_2$GeO$_4$:Mn, PL emission intensity increases compared to Zn free sample and PL peak excitation wavelength red-shifted with Zn addition. Both green and red emission is observed for Zn concentrations above 10 at% indicating the presence of Mn$^{2+}$ ions replacing Mg in Mg$_2$GeO$_4$ and Zn in Zn$_2$GeO$_4$. The phosphor can be used as an active layer in alternating current thin film electroluminescent (ACTFEL) devices.

References

14. JCPDS card no: 11-0687
15. JCPDS card no: 36-1479