CHAPTER 4

Growth and Characterization of Oxide Phosphor Thin Films
The present chapter deals with growth and characterization of oxide phosphor thin films and the chapter is divided into three parts. Part A deals with structural and optical characterizations of rf magnetron sputtered ZnGa$_2$O$_4$:Mn thin films. Thin films were deposited on glass/quartz at various substrate temperatures. The effect of a dopant source on structural and luminescent properties of ZnGa$_2$O$_4$:Mn thin films is discussed.

Part B discusses growth and characterization of Zn$_2$GeO$_4$:Mn thin films using rf magnetron sputtering. The effect of a ZnO buffer layer on structural and luminescent properties is discussed. It is observed that the presence of ZnO buffer layer enhances both crystalline quality and luminescent quality of Zn$_2$GeO$_4$:Mn films.

Part C deals with the growth and characterization of pulsed laser deposited Y$_2$O$_3$:Eu$^{3+}$ thin films. The effect of oxygen partial pressure and substrate temperature on structural and luminescent properties on deposited films is discussed. All the deposited films exhibit red luminescence with peak emission at 611 nm.
PART A

Growth and characterization of RF magnetron sputtered ZnGa$_2$O$_4$:Mn$^{2+}$ thin films
4A.1. Introduction

The future flat panel display (FPD) technologies demand highly efficient phosphor materials for better performance. Over a decade, oxide phosphors has been a subject of interest for their use in flat panel displays (FPD). Due to high thermal stability and long durability, oxide phosphors over-rule the commercially available and established sulphides, used in alternating current thin film electroluminescent (ACTFEL) displays [1,2]. Several binary and ternary oxide phosphors like Y$_2$O$_3$ [3], Ga$_2$O$_3$ [4, 5], ZnGa$_2$O$_4$ [6-10], Zn$_2$GeO$_4$ [11-17], Mg$_2$GeO$_4$ [18] etc have been extensively studied in bulk powder as well as in thin film form. Moreover high luminance green and red thick dielectric electroluminescent (TDEL) devices has been realized using doped ternary oxides like Zn$_2$SiO$_4$ [1], ZnGa$_2$O$_4$ [7-10] and Zn$_2$Si$_{(1-x)}$Ge$_x$O$_4$[19]. Among these ternary oxides, ZnGa$_2$O$_4$ is a low voltage cathodoluminescent (LVCL) phosphor that gives excellent green emission on Mn doping [20]. When excited by a 254 nm UV light, ZnGa$_2$O$_4$ exhibits blue emission due to its self activated luminescence [21]. It has Fd3m space group symmetry and crystallizes in the normal spinel structure with Zn$^{2+}$ ions occupying tetrahedral sites and Ga$^{3+}$ ions occupying octahedral sites. Zinc gallium oxide has a wide optical band gap of about 4.4 eV allowing tunability in the visible to UV range making it an ideal material for optoelectronic devices including FPDs, optical limiter for UV light and high temperature stable gas sensors [22]. Thin films of these compounds have been prepared using several techniques like rf magnetron sputtering [23-27], PLD [28-31], CVD [4] etc. Also white luminescence has been observed from ZnGa$_2$O$_4$:Dy$^{3+}$ bulk phosphor as well as thin films [32, 33]. Manganese has been used as an activator for obtaining high luminance green emission in these
compounds. In ZnGa$_2$O$_4$, Mn occupies tetrahedral Zn$^{2+}$ sites exhibiting green luminance at 507 nm due to transition via $^4T_1$-$^6A_1$ states of Mn$^{2+}$[34, 35]. Manganese can be introduced into host material via several compounds like MnO, MnCO$_3$, MnNO$_3$, MnSO$_4$, (CH$_3$COO)$_2$Mn etc. The dopant source does not affect the structure and luminescence of powder samples, but thin films of these samples were found to be sensitive to dopant source. Systematic studies on the optical and structural properties of rf magnetron sputtered ZnGa$_2$O$_4$:Mn thin films prepared using two targets, one doped with (CH$_3$COO)$_2$Mn and other with MnO, are carried out so that to control the optical and structural properties for desired application. For TDEL devices, high temperature post-deposition annealing above 1000°C is essential for getting good EL signal which eliminates the use of low temperature and economical substrates like glass. Significant lowering of the crystallization temperature and subsequent luminescent emission finds potential application in fabrication of ACTFEL devices using ZnGa$_2$O$_4$:Mn$^{2+}$ phosphor thin films on low temperature substrates like glass.

4A.2. Experiment

Thin films of ZnGa$_2$O$_4$:Mn$^{2+}$ were deposited on quartz substrates using rf magnetron sputtering technique. Stoichiometric powder target of Zn$_{0.98}$Ga$_2$O$_4$:Mn$_{0.02}$ was synthesized by solid state reaction of ZnO, Ga$_2$O$_3$ fired at 1350°C for 12 hrs and subsequent reduction in H$_2$ atmosphere for 3hrs at 900°C to reduce Mn$^{3+}$ and Mn$^{4+}$ to Mn$^{2+}$. Mn was doped in to the host material in two forms viz (CH$_3$COO)$_2$Mn and MnO with a dopant concentration of 2 at. %. The deposition was carried out at room temperature at an rf power of 125W in an Argon ambient of 0.015 mbar varying substrate to target (S-T) distance. Thin films were also deposited at various substrate temperatures keeping the S-T
distance at 4.5 cm. The films have thickness in the range 1.3-1.6 μm with a growth rate of 0.18 - 0.22 nm/s.

4A.3. Results and discussions

4A.3.1. X-ray diffraction studies

Figure 4.1 shows the XRD patterns of the films deposited (with (CH$_3$COO)$_2$Mn as dopant source) at various substrate to target (S-T) distances at room temperature. The standard reflections of the host are also shown for reference [61]. All the films are polycrystalline in nature except that deposited at higher S-T distances (6.5 cm and 7.5 cm). As the S-T distance increases the there is considerable variation in diffraction intensity from crystal planes of the films. At a S-T distance of 2.5 cm, the film has highest reflection intensity along (111) plane while at 3.5 cm highest diffraction intensity peak is (400) plane. At S-T distances 4.5 cm and 5.5 cm, the film has diffraction intensity maxima along the (311) direction. Beyond 5.5 cm, no traces of crystalline phases were found. Since the deposition time was kept constant, the thickness of the films was different (in the range 1.3-1.6μm). The orientation of the films mainly depends on two parameters viz background Ar pressure and S-T distance. Since background pressure is kept constant in our work, variation in S-T distance has a profound influence on the film texturing.

An accepted model based on thermodynamic considerations, is that there is a relationship between energy supplied to the adatoms during the film growth and different growth rates on different planes. In spinels (111) and (100) are the planes with lowest surface energy [35]. At shorter S-T distances, particles impinge on the substrate with higher energy producing films with (111)
and (100) orientation. The presence of Ar+ ions and other ionic species from the target have some influence on the transfer of energy of the adatoms.

Figure 4.1 XRD patterns of ZnGa$_2$O$_4$:Mn thin films (doped with (CH$_3$COO)$_2$Mn) at different S-T distances grown at room temperature. JCPDS of ZnGa$_2$O$_4$ is shown as reference.

The plasma interaction with the growing film and the energy of the adatom influence the growth of the film and hence texturing [36]. It is reported that the polycrystalline films with reflection intensity maximum along (311) plane shows excellent luminescent properties (discussed later). So in this study the S-T distance was kept at 4.5 cm. The surface energy of each plane plays an important role in texturing because surface area to volume ratio is large in thin films. If sufficient thermal energy is supplied, the films will thermodynamically grow with the densest direction.
Obviously the crystalline nature of the films at room temperature shows that the energy of the sputtered particles was high enough to orient along different direction without any additional thermal energy and the films are polycrystalline at different S-T distances.

The x-ray diffraction (XRD) pattern of films deposited at various substrate temperatures with (CH\(_3\)COO)\(_2\)Mn) as the Mn source in the target are shown in figure 4.2.

Figure 4.2 XRD patterns of ZnGa\(_2\)O\(_4\):Mn thin films (Mn source being (CH\(_3\)COO)\(_2\)Mn) at various substrate temperatures.
Figure 4.3 Variation of FWHM and lattice constant with substrate temperature of ZnGa$_2$O$_4$:Mn films deposited using (a) (CH$_3$COO)$_2$Mn as dopant source, (b) MnO as dopant source
The S-T distance was kept constant at 4.5 cm. All the films were polycrystalline with (311) reflection having maximum intensity. As the substrate temperature increases, the crystallinity improves which is evident from the increase in grain size. The full width at half maximum (FWHM) and lattice constant is found to decrease monotonously with substrate temperature and the variation is shown in figure 4.3a. The reduction in lattice constant gives rise to reduced cell volume. This could be due to re-evaporation of Zn at higher substrate temperatures giving rise to off-stoichiometric films with distorted structure.

Figure 4.4 shows the XRD patterns of the films deposited at various substrate temperatures, keeping the S-T distance at 4.5 cm, where the MnO was used for Mn doping in the target. Interestingly, the films exhibit entirely different structural and optical properties. The (311) peak is found to broaden with increase in substrate temperature. This broadening is expected due to the strain produced by uniform incorporation/substitution of Mn into the host lattice.

The films deposited using MnO as dopant compound, at room temperature, 500°C, 600°C and 650°C show highest reflection intensity along (311) orientation corresponding to spinel phase of ZnGa₂O₄. As the substrate temperature was increased to 700°C and 750°C, the films show orientation along (220) plane. In sputtering, the composition and properties of the deposited films is highly affected by 1) scattering angle differences of sputtered atoms, 2) sputtering yield of the target, 3) re-evaporation, 4) re-sputtering [31]. The factors 1, 2 and 4 mainly depend on the Ar pressure, RF power and the target composition. But in this study, the Ar pressure and RF power were kept constant through out. So it will not affect the film properties extensively. But the factor 3
is accelerated with substrate temperature. Therefore heating the substrate can give rise to Ga rich films, since the vapour pressure of Zn is high compared to Ga.

![XRD patterns of ZnGa$_2$O$_4$::Mn thin films (doped with MnO) at various substrate temperatures.](image)

Figure 4.4 XRD patterns of ZnGa$_2$O$_4$::Mn thin films (doped with MnO) at various substrate temperatures.

That is Ga/Zn ratio increases with an increase in substrate temperature which will produce off-stoichiometric films with uniform Mn distribution that in turn results in inferior crystalline films orienting along different crystal planes. The variation of FWHM of the films prepared, using the target with MnO as dopant, with substrate temperature is shown in figure 4.3b. It is observed that the FWHM increases with substrate temperature exhibiting an almost linear variation. The increase in FWHM of the (311) peak explicitly shows the smaller...
grain size and inferior crystallinity of the films. Similar observations were also reported by Minami et al. [4]. On the other hand, the lattice constant of the deposited films were found to be decreasing with substrate temperature implying the reduction of cell volume (fig 4.3b). This could be due to the increased Ga/Zn ratio as seen by XRF which will make distorted structure and results in cell volume reduction.

4A.3.2. Atomic Force Microscopy

Figure 4.5 AFM images of ZnGa$_2$O$_4$:Mn film deposited (a) at room temperature, (c) at 500°C, (e) at 600°C and (g) at 750°C and (b), (d), (f) and (h) shows corresponding topographies of image of (a), (c), (e) and (f).

Figure 4.5 shows AFM images of ZnGa$_2$O$_4$:Mn films (doped with MnO) deposited at various substrate temperatures. The images reveal granular shaped microstructure except for that deposited at room temperature. It is observed that roughness of the films increases (figure 4.6) as temperature increases. The film deposited at room temperature shows highly smooth with rms roughness of 3
nm. This is as expected as temperature increases re-crystallization takes place there by forming granular shaped micro particles increased roughness. The roughness of the films has a direct impact on the photoluminescence emission spectra which is discussed later.

![Graph showing variation in roughness of ZnGa$_2$O$_4$:Mn films (doped with MnO) with substrate temperature.](image)

Figure 4.6 Variation in roughness of ZnGa$_2$O$_4$:Mn films (doped with MnO) with substrate temperature

4A.3.3. Optical Characterization

(a) Transmission spectra

The transmission spectrum of the film (MnO as dopant) grown on quartz substrate at 600°C is shown in figure 4.7. All the films, irrespective of the dopant source used, show almost 90% transmission in the visible region and the band
gap calculated from the \((\alpha h\nu)^2\) vs \(h\nu\) plot (inset of fig. 5) lies in the range \(4.5 \pm 0.05\) eV which matches quite well with that of the bulk [32].

![Transmission spectra of ZnGa\(_2\)O\(_4\):Mn film deposited at 600°C. Inset shows \((\alpha h\nu)^2\) versus \(h\nu\) plot.](image)

**Figure 4.7** Transmission spectra of ZnGa\(_2\)O\(_4\):Mn film deposited at 600°C. Inset shows \((\alpha h\nu)^2\) versus \(h\nu\) plot.

(b) **Photoluminescence studies**

Figure 4.8 shows the PL emission and excitation (inset) of the reduced target powder (doped with manganese acetate) used for sputtering. The dopant concentration used is 2 at. %. The effect of concentration has been earlier studied and it is observed that ZnGa\(_2\)O\(_4\) with 2 at. % Mn shows maximum luminescent intensity [37]. The peak emission wavelength, when excited with 300 nm uv light was 504 nm which is consistent with the results obtained by several other authors [20, 38, 39]. The emission as observed from the spectra is
an asymmetric spectrum with a shoulder at 515 nm. The emission at 504 nm is attributed to $^4T_1 - ^6A_1$ transitions in Mn$^{2+}$ levels in which Mn$^{2+}$ ions is located at tetrahedral site (replacing Zn$^{2+}$) of the ZnGa$_2$O$_4$ host.

![Figure 4.8 Room temperature PL emission spectra of ZnGa$_2$O$_4$:Mn (2 at. %) phosphor (doped with (CH$_3$COO)$_2$Mn). Inset shows the corresponding excitation spectra](image)

But Mn can also replace Ga$^{3+}$ located at octahedral site which gives rise to shoulder at 515 nm [38]. The corresponding photoluminescent excitation spectra show a peak excitation wavelength at 300 nm which is the direct excitation of Mn$^{2+}$ ions. The peaks at higher wavelengths (425 nm, 450 nm and 460 nm) can also be attributed to the direct excitations of Mn$^{2+}$ ions in the
lattice. This also proves that Mn$^{2+}$ has been incorporated into the ZnGa$_2$O$_4$ host and it replaces tetrahedral Zn$^{2+}$ ions as well as Ga$^{3+}$ ions.

The PL emission and excitation (inset) spectra of the target phosphor doped with MnO is shown in figure 4.9.

![Figure 4.9 Room temperature PL emission spectra of ZnGa$_2$O$_4$:Mn (2 at. %) phosphor (doped with MnO). Inset shows the corresponding excitation spectra](image)

The emission and excitation spectra have similar characteristics as that doped with manganese acetate. The luminescence emission band gives some information about the oxidation state of the dopant ions. Green emission at 507 nm can be attributed to the $^4T_1 \rightarrow ^6A_1$ transition in Mn$^{2+}$ ions situated at tetrahedral site symmetry [38]. The as-prepared bulk powder phosphors, before
reduction, did not exhibit intense green emission. This is due to the fact that at high temperatures there is a strong chance for the oxidation of Mn$^{2+}$ into Mn$^{3+}$ and in order to balance the charge it will migrate to octahedral site. This Mn$^{3+}$ will absorb the green emission from the Mn$^{2+}$ ions at tetrahedral position due to charge transfer between them [34]. The presence of Mn$^{2+}$ at tetrahedral site is essential for an efficient luminescence from the phosphor. The green PL emission after reduction, in both phosphor targets confirms that Mn is incorporated in to the host lattice as Mn$^{2+}$ at tetrahedral site.

![Graph](image)

$\lambda_{\text{exc}} = 290$ nm

Figure 4.10 Room temperature PL emission spectra of ZnGa$_2$O$_4$:Mn thin films [(CH$_3$COO)$_2$Mn as dopant source].

The films deposited using the phosphor with (CH$_3$COO)$_2$Mn as dopant source did not show any luminescence (figure 4.10 shows the high level of
noise) even though enough thermal energy was supplied during film growth via substrate heating. The spectrum doesn’t show any characteristics of ZnGa₂O₄:Mn phosphor. In order to probe whether the luminescence was killed by the presence of Mn³⁺ ions, the films were post-annealed in H₂ atmosphere at 800°C to reduce Mn³⁺ ions, if any in the samples. Still no luminescence could be observed from the films. This points towards improper/no incorporation of Mn into the host lattice resulting in absence of luminescence in the films deposited using (CH₃COO)₂Mn as dopant source. The reduction in FWHM (Fig 4.3a) also implies that substrate heating contributed only towards improvement of crystallinity of the films.

![Graph showing PL emission spectra at various substrate temperatures.]

Figure 4.11 Room temperature PL emission spectra of ZnGa₂O₄:Mn thin films (MnO as dopant source) at various substrate temperatures.
The films deposited with MnO as the dopant source in the target gives green emission similar to the bulk phosphor. Figure 4.11 shows the room temperature PL emission spectra of ZnGa$_2$O$_4$:Mn thin films deposited at various substrate temperatures. All the films gave green emission band, with peak at 508nm attributed to the $^{4}T_{1} \rightarrow ^{6}A_{1}$ transition of tetrahedrally coordinated Mn$^{2+}$ ions. The spectra also show a broad host emission band peaking at 421 nm due to the self-activated luminescence. In ZnGa$_2$O$_4$, Ga$^{3+}$ acts as sensitizer [21].

The mechanism of luminescence in ZnGa$_2$O$_4$:Mn$^{2+}$ is identified as non-radiative resonant energy transfer with electric dipole-dipole interaction between sensitizer (Ga$^{3+}$) and activator (Mn$^{2+}$) ions as there is significant overlap of the activator absorption and sensitizer emission [23]. The film deposited at room temperature, though polycrystalline in nature, didn’t exhibit any luminescence. But the films deposited at and above 500°C exhibit green emission which is a clear indication of the diffusion of Mn$^{2+}$ ions at higher temperatures. As the substrate temperature increases, PL emission intensity increases, reaches a maximum for 600°C and then decreases at higher substrate temperatures.

The luminance properties of phosphors depend strongly on grain size, Zn/Ga ratio and crystal structure. Luminescence efficiency of high voltage phosphors decrease with reduced grain size due to photon absorption and scattering. For low voltage phosphors like ZnGa$_2$O$_4$, high luminescent efficiency is observed with reduced grain size due to larger surface area per unit volume [31]. Moreover, it has been reported that slightly Zn deficient films exhibit superior luminescent characteristics due to enhanced Mn$^{2+}$ substitution at Zn tetrahedral sites [23]. In the present work, FWHM is observed to increase with
substrate temperature (evident from figure 4.3b) and subsequent reduction in grain size enhances luminescence. In addition, Zn/Ga ratio of the films reduces with substrate temperature, vapor pressure of Zn being higher compared to Ga. Excess Ga sites also serve as activators in these films. Beyond 600°C, growth along other crystal planes is promoted reducing the PL intensity, in spite of reduced grain size. In the case of substrate temperatures above 650°C, the (311) spinel orientation is lost. It has been reported that the films with (311) orientation show superior luminescence characteristics than any other orientation [34]. Moreover, the films grown at higher substrate temperature are highly Zn deficient favoring the formation of monoclinic β-Ga₂O₃ phase which will again reduce the PL intensity.

The PL emission intensity and peak emission wavelength of the host shows random variation with temperature. The luminescent intensity and peak emission wavelength of the host relates to Zn/Ga ratio and Ga-O ligand strength [39]. As temperature increases, host emission decreases up to 650°C and above 650°C it varies at random. This is due to the fact that above 650°C, there is a considerable variation in the crystal structure of the host and there is also considerable re-evaporation of Zn at temperatures above 650°C [39]. Due to the increase in density of Zn vacancies, at high temperatures, Ga³⁺ migrates from octahedral sites to tetrahedral sites forming distorted octahedral structure in the spinel [21]. This will considerably alter the host emission wavelength, intensity and corresponding transfer of energy resulting in considerable variation of luminescence output.
4A.3.4 The CIE Coordinates

Figure 4.12 CIE coordinates of the PL emission spectra of ZnGa$_2$O$_4$:Mn thin films

The CIE coordinates of the PL emission spectra is shown in the figure 4.12. The coordinates lie in the bluish-green region of the coordinate diagram. The bluish color corresponds to contribution from the host.

Conclusion

In summary Mn doped zinc gallate phosphor have been synthesized using different Mn precursors namely, manganese acetate and manganese oxide. The influence of these precursors on structural and optical properties of thin films prepared using targets (Zn$_2$GaO$_4$:Mn), one doped with (CH$_3$COO)$_2$Mn and other with MnO has been investigated. Even though the powder targets do not
show any variation in structural and optical characteristics, thin films prepared from these targets show different characteristics. FWHM of the x-ray diffraction peak (311) is found to decrease with substrate temperature when the dopant source was \((\text{CH}_3\text{COO})_2\text{Mn}\) but the films deposited using MnO as dopant source in the target, FWHM increases with substrate temperature. The use of MnO results in uniform substitution of Mn in the host lattice which in turn gives rise to broadening of FWHM. No luminescence was observed when acetate was used as dopant implying the fact that Mn is not incorporated in to the host lattice, in the film even though the target showed excellent green emission. In the sight of structural and optical characteristics it is concluded that manganese oxide is better choice of doping Mn rather than manganese acetate.
PART B

Growth and Characterization of RF magnetron sputtered $\text{Zn}_2\text{GeO}_4:\text{Mn}^{2+}$ thin films
Growth and Characterization of Zn$_2$GeO$_4$:Mn$^{2+}$ thin films

4B.1. Introduction

Zn$_2$GeO$_4$ doped with Mn is known to emit green light up on UV excitation. Zn$_2$GeO$_4$ has rhombohedral structure, similar to Zn$_2$SiO$_4$, with Zn ions at tetrahedral sites and Ge at octahedral sites and have a wide band gap of 4.68 eV [12, 13]. Undoped Zn$_2$GeO$_4$ phosphor is a native defect phosphor and exhibits white luminescence under UV excitation [17]. Mn$^{2+}$ substitutes for Zn$^{2+}$ in the host and a green emission is obtained via a transition between $^4T_1$-$^6A_1$ levels of Mn$^{2+}$. Thin films of Zn$_2$GeO$_4$ have been deposited using pulsed laser deposition (PLD) [11], RF magnetron sputtering [12-14] etc and they find application as CL phosphor and EL phosphor. Thick dielectric electroluminescent (TDEL) and alternating current thin film electroluminescent (ACTFEL) devices with Zn$_2$GeO$_4$ as active layer has also been developed [14, 15]. This phosphor has also been investigated for integrated optics applications [17].

Unfortunately, one of the fundamental problems of oxide thin-film phosphors is their inferior luminous efficiency and brightness when compared to their powder form. The inferior luminescent properties are caused by internal reflection from the planar interface, the so-called ‘‘light-piping effect,’’ and inferior crystallinity [3, 40]. The luminescent output can be improved by either increasing the light-scattering centers by surface modification or by reducing defects after post-annealing at high temperatures [3, 41]. In most studies post deposition annealing (RTA, hydrothermal or furnace anneal) is carried out to improve the luminescent (PL, EL or CL) characteristics of the phosphor layer [11-15]. The high crystallization temperature of oxide phosphors also prevent them from being deposited on cheaper glass substrates. Thick dielectric
substrates like BaTiO$_3$ and high temperature post deposition annealing is usually employed to improve crystalline quality of the thin film. However Lewis et al. [12] has developed TFEL devices using Zn$_2$GeO$_4$:Mn as active layer on glass substrates through RTA treatments. The crystallization temperature of Zn$_2$GeO$_4$:Mn is found to be 650°C [13] and better crystalline films are obtained only after post-deposition annealing of the films. The inferior crystallinity of the as-deposited, polycrystalline thin-film phosphors are mostly due to a limitation of the amorphous like substrates used. Moreover, it is hard to reduce the defect density in phosphor films by a post-annealing process at high temperatures due to low softening temperature of the glass substrate. One of the possible methods to obtain polycrystalline thin-film phosphors with enhanced crystallinity is by growing phosphor layer over a highly crystallized buffer layer which is grown on the amorphous substrate. The ZnO thin film is chosen as the buffer layer because it is relatively easy to grow a high quality crystalline film.

In this work, the dependence of Zn$_2$GeO$_4$:Mn thin film growth on deposition parameters like RF power and substrate temperature and the influence of ZnO buffer layer on the structural and optical characteristics of Zn$_2$GeO$_4$:Mn thin films has been investigated.

4B.2. Experiment

Thin films of Zn$_2$GeO$_4$:Mn$^{2+}$ were deposited on quartz substrates by RF magnetron sputtering (2" gun). The target used was Zn$_2$GeO$_4$:Mn$^{2+}$ powder prepared by the solid state reaction of constituent oxides. The starting materials, namely ZnO (99.99%, Alfa Aesar), GeO$_2$ (99.99%, Alfa Aesar) and MnO (99.99%, Alfa Aesar), were mixed stoichiometrically in ethanol medium and
then fired at 1200°C for 12hrs. The doping concentration was fixed at 2 at. %. The deposition was carried out on the substrate kept at 4.5cm away from the target in an Ar ambient of 0.015 mbar at various RF powers for one hour. The ZnO buffer layer (~ 100 nm) was deposited at a substrate to target distance of 4.5 cm in an Ar ambient of 0.015mbar at 400°C for 3 minutes. The RF power was kept at 100 W (28 W/cm²). The phosphor layer was then deposited on ZnO/Quartz at various substrate temperatures varying from room temperature to 700°C. The thickness of the samples was measured using Dektak 6M stylus profiler and the average growth rate of phosphor layer was found to be 0.2nm/s. The crystal structure of the films was analyzed using Rigaku x-ray diffractometer using Cu Kα radiation (1.5414Å). The transmission spectra were recorded using JASCO V-570 spectrophotometer. Room temperature photoluminescence (PL) emission and excitation spectra (PLE) were recorded using Jobin Yvon Fluoromax-3 spectrometer equipped with a 150W xenon lamp. The surface morphology of the films were analyzed using scanning electron microscope (SEM).

4B.3. Results and discussions

4B.3.1 X-ray diffraction studies

The XRD patterns of Zn₂GeO₄:Mn²⁺ films deposited on quartz substrates for various RF powers are shown in figure 4.13. The substrate was heated to 650°C prior to deposition. The films deposited at the RF powers 100W and 125W did not show any crystallanity. But when the RF power was raised to 150W, polycrystalline films were grown. The peaks of x-ray diffraction pattern
matched well with the standard reflections of the rhombohedral Zn$_2$GeO$_4$ host [62].

Figure 4.13. xrd patterns of Zn$_2$GeO$_4$:Mn thin films deposited at 650°C on quartz substrates at various RF powers. The JCPDS of Zn$_2$GeO$_4$ host and xrd pattern of target (Zn$_2$GeO$_4$:Mn) is given for reference.

In sputtering, the composition and properties of the deposited films is highly affected by 1) scattering angle differences of sputtered atoms, 2) sputtering yield of the target, 3) re-evaporation, 4) re-sputtering [25]. The factors 1, 2 and 4 mainly depend on the Ar pressure, RF power and the target composition and factor 3 depends on substrate temperature. Since background Ar pressure and target composition are constant throughout this experiment, RF power and substrate temperature has profound influence on the crystalline
quality of the films. The presence of Ar\(^+\) ions and other ionic species from the target also have some influence on the transfer of energy of the adatoms. The surface energy of each plane plays an important role in texturing because the surface area to volume ratio is large in thin films. If sufficient thermal energy is supplied, the films will thermodynamically grow with the densest direction. Here, polycrystalline films could be grown only when the RF power was raised to 150 W at a substrate temperature 650\(^\circ\)C. It should be inferred that under these conditions, the sputtered particles had the sufficient thermal energy to favour the film growth thermodynamically. Interestingly, crystallinity couldn’t be observed for the films deposited at lower substrate temperatures (500\(^\circ\)C, 600\(^\circ\)C) or at lower RF powers (100 W, 125 W).

The XRD patterns of ZnO buffer layer grown at 400\(^\circ\)C is shown in figure 4.14. The rf power used was 100 W. Inset shows variation in FWHM of (002) peak of ZnO with annealing temperature after deposition at 400\(^\circ\)C. A minimum FWHM was observed for annealing temperatures 600\(^\circ\)C and 650\(^\circ\)C showing that better crystalline films are obtained at these temperatures.

Figure 4.15 shows the XRD patterns of Zn\(_2\)GeO\(_4\):Mn thin films deposited on ZnO/quartz substrate at various substrate temperatures. The oriented growth of ZnO buffer layer along the (002) plane is observed in all cases. At 500\(^\circ\)C and 550\(^\circ\)C, the reflections from the Zn\(_2\)GeO\(_4\):Mn layer were absent. As the temperature reached 600\(^\circ\)C, reflection from (220) plane of Zn\(_2\)GeO\(_4\) is observed and a sudden increase in the reflection intensity takes place when the substrate temperature is 650\(^\circ\)C. At 700\(^\circ\)C polycrystalline film is formed. All these reveal that the crystalline ZnO surface presents a better platform for thin film growth rather than an amorphous substrate.
When a film is grown on a crystalline surface, the resulting film may be influenced by the initial surface. If the underlying crystal structure of the film/substrate is compatible with that of the phosphor film, and if the temperature is sufficiently high to enable reorganization of the deposited atoms, one can enhance the structural properties of the latter. Or else, along with energy of sputtered material, additional thermal energy is needed to crystallize the film.
Figure 4.15. XRD patterns of Zn$_2$GeO$_4$:Mn thin films deposited on ZnO/quartz substrates at various substrate temperatures and on amorphous quartz substrate at 600°C.

* represents (002) plane of ZnO.

Here, the presence of the ZnO buffer layer assists the formation of highly oriented Zn$_2$GeO$_4$:Mn$^{2+}$ films even at a substrate temperature of 600°C. The growth of (220) plane at 600°C and 650°C could be due to unfavourable interfacial energy between (410) plane of Zn$_2$GeO$_4$ and (002) plane of ZnO while at 700°C, the films are highly poly crystalline due to relaxation of ZnO buffer layer at higher temperature. At this point, it is worth mentioning that films deposited without the ZnO buffer have quite different structural properties. The full width at half maximum (FWHM) of the (220) peak of Zn$_2$GeO$_4$:Mn was found to be 0.23° and 0.29° with and without the buffer layer respectively. This
is suggestive of the fact that the presence of a highly crystallized buffer layer also enhances the crystallinity of the phosphor films and helps in film texturing.

**4B.3.2 Band gap**

The band gap of the films was determined using the Tauc plot \((\alpha h\nu)^2 \text{ vs } h\nu \text{ curve}\). Figure 4.16 represents the Tauc plot of the Zn2GeO4:Mn films grown at 650°C with and without ZnO layer.

![Tauc plot graph](image)

Fig.4.16. \((\alpha h\nu)^2 \text{ vs } h\nu \text{ plot (Tauc plot) of } Zn_2GeO_4:Mn \text{ thin film deposited on a) } ZnO/quartz \text{ and b) amorphous quartz substrate. Inset shows corresponding PL emission from a) } Zn_2GeO_4:Mn/ZnO/quartz \text{ and b) } Zn_2GeO_4:Mn/quartz \text{ films.}"

The film without the ZnO buffer layer has quite discrete sub-band gap absorption at 3.5 eV in addition to the band to band absorption of the host at 180
4.57 eV. But for the film grown with ZnO buffer layer, the curve exhibits a linear behavior with a different slope at energies above the sharp sub-band gap absorption (at 3.5 eV) attributed to phonon-assisted absorptions. The sub-band absorption is due to the formation of oxygen vacancies, the presence of which is intrinsic in film deposition process. Moreover, the evaporation of Zn at high substrate temperature increases Zn defects in the film which in turn generate oxygen vacancies via Ge$^{3+}$ migration to vacant tetrahedral Zn sites, to avoid charge imbalances (which is observed in bulk phosphor also). The increased defect density in the Zn$_2$GeO$_4$:Mn/ZnO films improves the spectral overlap between the sub band states and excited levels of Mn$^{2+}$. This enhances the resonant energy transfer from the host to the activator thereby increasing the intensity of the green luminescent emission.

4B.3.3 Scanning electron microscopy

The microstructure of the deposited films was analyzed using scanning electron microscope (figure 4.17). Film deposited on bare quartz substrate at 650°C and that on ZnO/quartz substrate at 700°C shows similar surface morphology with octahedral shaped particles. Film deposited on ZnO/quartz substrate at 500°C and 600°C were smooth. But the film deposited at 650°C shows coffee bean shaped particles which is quite different morphology compared to all other films. For high voltage phosphors, generally luminance intensity falls with reduced grain size, due to photon scattering and absorption. Further more, roughness of the film surface also enhances luminance output. Here films deposited on bare quartz and on ZnO/quartz at 700°C are rough than that deposited on ZnO/quartz substrate at 650°C.
Figure 4.17. SEM images of Zn$_2$GeO$_4$:Mn thin films deposited (a) on bare quartz substrate at 650°C, on ZnO/quartz substrate at (b) 500°C, (c) 650°C and (d) 700°C.

But grain size of film grown at 650°C is higher than the other films grown on quartz at 650°C and ZnO/quartz at 700°C. Enhanced luminance output was observed from the film grown on ZnO/quartz at 650°C (discussed below) which also resulted in enhanced crystalline quality of the film. At 700°C, the increased thermal energy causes surface boiling of the buffer layer significantly. Consequently the chemical loss from the buffer layer prevents grains from merging, and thus surface morphology of the film looks as if there is no buffer layer at all.
4B.3.4 Photoluminescence studies

The PL emission intensity varies drastically with substrate temperature (figure 4.18) which also depicts the fact that PL intensity highly depends on crystallinity of the films. The maximum intensity is observed for that deposited at 650°C. The emission at 540 nm corresponds to transition from $^4T_1 - ^6A_1$ of Mn$^{2+}$ levels with tetrahedral configuration. Mn$^{2+}$ is supposed to replace tetrahedral Zn in Zn$_2$GeO$_4$. The crystal field has profound effect on the luminescence of Mn$^{2+}$ in crystals. As crystalline Zn$_2$GeO$_4$ is only formed at a substrate temperature of 650°C, the luminescence intensity peaks for the film deposited at this critical temperature. However at 700°C, the luminescent intensity decreases. Apart from crystallinity the composition of the films also influence the luminescent intensity of the films. Since the vapour pressure of Zn is high, at elevated substrate temperatures, there is severe chance for the re-evaporation of Zn and in most cases the films will be Zn deficient. This will certainly affect the crystal field of Mn$^{2+}$ which influences the luminescent intensity. The mechanism of luminescence is identified as a resonant transfer from a sub-band state which lies nearly 1 eV below the conduction band to Mn$^{2+}$ levels. Any perturbation of this level will seriously affect the luminescent intensity. As Zn vacancies are more at higher substrate temperature, this sub band state is perturbed more, there by reducing the resonant energy transfer and luminescence output.

The PLE spectra of the films are shown in the figure 4.19. The spectra show a blue shift with respect to increase in substrate temperature. In the bulk phosphor the excitation corresponding to 540 nm emission is 332 nm. For the films deposited at 600°C, PLE peak excitation wavelength is 332 nm. However
inferior crystalline nature of the film reduced the luminescence output. As we increase the temperature, more Zn vacancies are formed and PLE is blue shifted to 308 nm and for films deposited at 700°C the PLE peak excitation wavelength is at 303 nm.

![Graph](image)

Figure 4.18. Room temperature PL emission spectra of Zn$_2$GeO$_4$:Mn thin films deposited on ZnO/quartz substrates at various substrate temperatures.

This excitation is consistent with the sub-band absorption observed from Tauc plot indicating that resonant transfer of energy occurs from sub-band states. This blue shift is direct consequence of reduced Zn/Ge ratio which will considerably increase the defect density of the host.
Conclusion

In summary, Zn$_2$GeO$_4$:Mn thin films were deposited on quartz substrates at various substrate temperatures with out any post deposition annealing. The effect of RF power, substrate temperature and ZnO buffer layer on structural and luminescent characteristics of the films was studied in detail. At 650°C and RF power of 150 W, polycrystalline films could be grown on quartz substrates. Texturing along (220) direction is observed for films grown on ZnO/Quartz. Sharp sub band absorption at 3.5 eV and band edge absorption at 4.57 eV is
observed for film grown on bare quartz substrate while only strong sub band absorption was observed for film grown on ZnO/Quartz substrate indicating higher defect density in latter films. Photoluminescent emission was found to be enhanced for the film deposited on ZnO/Quartz substrate, at 650°C, than that deposited on bare quartz substrate. PLE was found to blue shift with substrate temperature.
PART C

Pulsed Laser Deposition of $\text{Y}_2\text{O}_3$:Eu thin films
4C.1. Introduction

Thin films of Y$_2$O$_3$ has been of a great research interest over last few years due to its wide application potential such as metal insulator-semiconductor (MIS) diodes, metal-oxide semiconductor capacitors (MOS), Dynamic random access memory (DRAM) gate dielectric because it possess a wide band gap (5.8 eV), high dielectric constant [42-46] and high melting point (2410°C). It has also been used as a dielectric layer in thin film electroluminescent (TFEL) displays [47]. However in fluorescent lamps and cathodoluminescent displays, Eu doped Y$_2$O$_3$ acts as a phosphor emitting red light. In energy saving lamps it is used as a powder with a grain size of several microns, combining high quantum efficiency, a proper emission wavelength, and a large absorptivity for the exciting radiation. Enhanced emission intensity and efficiency has been observed via co-doping Y$_2$O$_3$:Eu with Zn, Gd, Li, La [43-46, 48]. Blue green and red cathodoluminescence were also observed from doped Y$_2$O$_3$ thin films prepared using sol-gel process making it a suitable material for electroluminescent and cathodoluminescent phosphor [49]. Thick dielectric electroluminescent devices were also fabricated on ceramic substrates using Y$_2$O$_3$:Mn as active layer [50]. In Y$_2$O$_3$:Eu$^{3+}$, the mechanisms that are governing the absorption which also gives rise to red emission are 1) direct excitation of the Eu$^{3+}$ ion, 2) excitation via a charge-transfer state between the Eu ion and neighboring O ions or 3) excitation via the Y$_2$O$_3$ host lattice [51]. In Y$_2$O$_3$: Eu, emission consists of large number of lines ranging from 580 – 700 nm and in general these lines can be assigned to $^5$D$_0$ - $^7$F$_J$, J=0,1,2,3 transitions. Each of these transitions is partially resolved in to various m$_J$ transitions. All of these emission lines corresponds to inner f-f transitions and are electric dipole
forbidden. From the emission spectrum, once can speak about local crystal environment of Eu$^{3+}$ ion, especially from the relative intensity ratio of $^5D_0 - ^7F_1$ and $^5D_0 - ^7F_2$ emission lines. Because the intensities of these transitions highly depend on local crystal environment in different ways [52]. The $^5D_0 - ^7F_1$ transition is electric dipole forbidden and intensity of this line can be attributed to magnetic dipole operator and almost insensitive to local environment. But $^5D_0 - ^7F_2$ transition, by mixing with higher allowed transition, is electric dipole allowed and intensity of which being hypersensitive to local environment (ie, the local electric field and local symmetry) [53].

Pulsed laser deposition (PLD) has been widely used to deposit high quality thin films. Single crystal substrates like sapphire, LaAlO$_3$ (for epitaxial growth), Si etc has been used to grow high quality crystalline thin films [40, 54-56]. More over thin films offer better adhesion to solid surface, higher lateral resolution, better thermal stability and reduced out-gassing compared to phosphors in bulk powder form. But lower brightness and efficiency of thin films, due to internal reflection, small interaction volume and absorption of light by substrate material, are rather its negatives. Further more the structural and optical characteristics of thin films grown, highly depends on the properties of substrate chosen. Therefore, usually single crystalline substrates are used for phosphor thin film deposition. On the other hand these single crystalline substrates are expensive which prevents commercialization of devices fabricated on them. So it is advisable to use cheaper amorphous substrates like glass or fused silica for deposition of thin film phosphors.

In the present work Y$_2$O$_3$:Eu$^{3+}$ thin films have been deposited on amorphous fused silica substrates using pulsed laser deposition and the films has
been characterized structurally and optically. $Y_2O_3$ thin films were deposited using rf magnetron sputtering at various rf powers. But sputtering rate was very low (average of 0.035 nm/sec) so that we could get a 100-150 nm thick film when sputtered in the range 150 -200 W rf power (maximum available power in the rf unit) at a substrate distance of 4 cm. Therefore in order to get thicker films sputtering has to be performed for quite long time which was not feasible. Laser ablation technique has been found to have higher growth rate and hence PLD was used to grow $Y_2O_3$:Eu thin films.

4C.2. Experiment

Thin films of $Y_2O_3$:Eu$^{3+}$ were deposited on quartz substrates using pulsed laser deposition (PLD). The target of $Y_{1.96}O_3$:Eu$_{0.04}$ was synthesized by solid state reaction of $Y_2O_3$ and Eu$_2O_3$ fired at 1200°C for 12hrs and sintered at 1450°C for 48 hrs. The synthesized target was ablated using 4th harmonic Nd:YAG laser of wavelength 266 nm with a repetition frequency of 10 Hz and pulse duration 6 ns. Thin films were deposited at various substrate temperatures keeping the S-T distance at 4 cm and at an oxygen partial pressure of $10^{-4}$ mbar. Films were also deposited at various oxygen partial pressures at a substrate temperature of 600°C and S-T distance of 4 cm. The laser fluence was kept constant through out at 2 J/cm$^2$. The thickness of samples was measured using Dektak 6M stylus profiler. The films have thickness in the range 750-900 nm with a growth rate of 0.2-0.25 nm/s. The crystal structure of the films was analyzed using Rigaku x-ray diffractometer employing a Cu K$_\alpha$ radiation (1.5414Å). The transmission spectra were recorded using JASCO V-570 UV-Vis-NIR spectrophotometer. Room temperature photoluminescence emission (PL) and excitation spectra (PLE) were recorded using Horiba Jobin Yvon Fluoromax-3 spectrometer.
equipped with 150W xenon lamp. The morphology of the films was analyzed using a scanning electron microscope (SEM).

4C.3 Results and discussions

4C.3.1 X-ray diffraction studies

Figure 4.20 shows xrd patterns of Y₂O₃:Eu thin films deposited at various oxygen partial pressures (PO₂) at a substrate temperature of 600°C. All the films were oriented along (222) plane which is the lowest surface energy plane. It is quite interesting that such high quality thin films are formed on amorphous substrates like quartz even though with substrate heating.

![XRD patterns of Y₂O₃:Eu thin films deposited at various PO₂; Tₛ = 600°C](image)

Figure 4.20. XRD patterns of Y₂O₃:Eu thin films deposited at various PO₂; Tₛ = 600°C
The variation of Full width at half maxima (FWHM) and lattice constant with PO\textsubscript{2} is shown in figure 4.21. FWHM decreases with increase in PO\textsubscript{2}, reaching a minimum of 0.17° for film deposited at 0.05mbar PO\textsubscript{2} and then increases with increase in partial pressure. However lattice constant increases with PO\textsubscript{2} reaching maximum for 0.05mbar and then decreased.

![Graph showing variation of FWHM and lattice constant with PO\textsubscript{2}](image)

Figure 4.21. Variation of FWHM and lattice constant with PO\textsubscript{2}

Generally laser ablation of oxides in vacuum results in oxygen deficient films and in order to compensate the oxygen loss, deposition is carried out in oxygen ambient. Moreover, oxides that are highly sensitive to oxygen content, structural variations or deformations are also observed [57]. It is observed that similar to reduction in oxygen content, excess oxygen content will also create some defect levels in the lattice. In this case an optimum PO\textsubscript{2} of 0.05 mbar is observed below and beyond which, crystallinity is decreased (FWHM increases). Interestingly at this pressure, lattice constant is observed to be
maximum, which is close to the bulk value or strain is found to be minimum at this optimum partial pressure of oxygen. Therefore similar to oxygen deficiency, excess oxygen content will also give rise to distortions in crystal structure. In bulk Y$_2$O$_3$, it is observed that the activator incorporation degree (AID) has direct influence on lattice parameter \cite{58}. Nazarov \textit{et al.} \cite{58} observed that there is a linear dependence between activator incorporation degree and lattice parameter. Moreover particle size also contributes to the activator incorporation. Therefore from the figure 4.21 it is clear that observed maximum value of lattice constant is for film deposited at 0.05 mbar pressure that have minimum FWHM (maximum grain size).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{xrd_patterns}
\caption{XRD patterns of Y$_2$O$_3$:Eu thin films deposited at various substrate temperatures; PO$_2$ = 10^{-4} mbar}
\end{figure}
This suggests a correlation between activator incorporation degree, oxygen partial pressure and particle size. At an optimum oxygen partial pressure; activator incorporation is high with an increased grain size. Figure 4.22 shows the xrd patterns of films deposited at 10^{-4} mbar at various substrate temperatures. All the films were oriented along (222) plane showing that highly crystalline films could be grown even at a substrate temperature of 300°C on amorphous quartz substrates. As the temperature increases FWHM of the (222) peak reduces thereby increasing the crystalline quality of the deposited films. The superior crystalline quality at higher substrate temperatures could be due to the increased grain size which is often observed in high temperature thin film deposition.

**4C.3.2 Scanning electron microscopy**

Figure 4.23 shows SEM pictures of film deposited at various deposition conditions. (a), (b) and (c) shows the films deposited at 0.0001 mbar, 0.5 mbar and 0.1 mbar P_0^2, at a substrate temperature of 600°C. Fig 4.23 (d) shows that deposited at 0.0001 mbar and 300°C substrate temperature. It is obvious that the film deposited at 0.05 mbar P_0^2 and 600°C shows highest crystallite size and surface looks rougher than in the other films. This is consistent with the FWHM analysis from xrd pattern as minimum FWHM is obtained for this film. Substrate temperature also has similar effect on surface morphology of as deposited thin films. As temperature increases film become more rough and crystalline. Figure 4.24 show the SEM of film deposited on quartz substrate at 700°C and 0.0001 mbar P_0^2.
Figure 4.23. SEM micrographs of Y$_2$O$_3$:Eu thin films deposited at (a) 600°C, 10$^{-4}$ mbar PO$_2$, (b) 600°C, 0.05 mbar PO$_2$, (c) 600°C, 0.1 mbar PO$_2$ and (d) 300°C, 10$^{-4}$ mbar PO$_2$

Figure 4.24. SEM micrographs of Y$_2$O$_3$:Eu thin films deposited at 700°C, 10$^{-4}$ mbar
4C.3.3 Photoluminescence studies

Figure 4.25. PL emission spectra of Y$_2$O$_3$:Eu thin films deposited at 0.1 mbar oxygen partial pressure. Inset shows the variation in integral intensity with PO$_2$; $T_s = 600^\circ$C

Figure 4.25 shows PL emission spectra of Y$_2$O$_3$:Eu films deposited at various oxygen partial pressure and at a substrate temperature of 600$^\circ$C. The PL intensity was found to increase with increase in oxygen partial pressure. Thicknesses of the films were also found to increase with PO$_2$. The variation in deposition rate with PO$_2$ is shown in figure 4.26. This was quite different from the results obtained for Zhang et al. [59] as they observed a decrease in thickness for films deposited at higher PO$_2$ (The pressure range used by them was 0.01 - 0.1 mbar). They had also observed that the energetic plume created by the laser
ablation became shorter and narrower as the gas pressure (PO$_2$) in the deposition chamber was increased [59]. In the present study, we observed an increase in plume density and length with increase in PO$_2$.

![Graph showing variation of deposition rate of Y$_2$O$_3$ thin films with PO$_2$](image)

**Figure 4.26.** Variation of deposition rate of Y$_2$O$_3$ thin films with PO$_2$

The increase in plume intensity accompanied by an increase in emission intensity was also observed in our earlier studies in ZnO plasma [60]. With the increase in oxygen partial pressure, an increase in the density of Zn neutrals was observed [60]. In conjunction to that, an increase in Y neutrals might have occurred with the increase in PO$_2$ which resulted in increased plasma emission intensity. The differences in the results with Zhang et al. [59] may be due to the difference in laser fluence (Zhang et al. used a laser fluence of 5.2 J/cm$^2$) used.
Moreover they observed shortening of plasma plume with increase in PO₂ while we observed an increase of the plasma plume.

Figure 4.27 shows PL emission spectra of films deposited at 10⁻⁴ mbar at various substrate temperatures.

![Figure 4.27. PL emission spectra of Y₂O₃:Eu thin films deposited at 700°C. Inset shows the variation in integral intensity with substrate temperature; PO₂ = 10⁻⁴ mbar](image)

The PL shows highly resolved spectrum of Eu³⁺, intensity maximum being observed at 615 nm. The peak emission can be attributed to ⁵D₀ - ⁷F₂ transition in C₂ symmetry. The mechanisms that are responsible for the PL emission are 1) direct excitation of the Eu³⁺ ion 2) excitation via a charge-transfer state between the Eu ion and neighboring O ions and 3) excitation via...
the Y\textsubscript{2}O\textsubscript{3} host lattice. Eu\textsuperscript{3+} ions are supposed to replace Y\textsuperscript{3+} ions in the host lattice, thereby creating a charge transfer state (CTS) with neighboring oxygen atoms. These CT states absorb light from the incoming radiation, from which resonant transfer takes place to Eu\textsuperscript{3+} ions resulting in corresponding red PL emission. The emission spectrum consists of several lines which gives information about Eu\textsuperscript{3+} site symmetry in the lattice. In Y\textsubscript{2}O\textsubscript{3}, each Yttrium atoms are surrounded by six oxygen atoms (instead of eight) making it intrinsically a defect phosphor.

These defects can be along body diagonal (C\textsubscript{2} symmetry), or along face diagonal of a cube (S\textsubscript{6} symmetry) [42]. Only 1/3\textsuperscript{rd} of the Y atoms occupy S\textsubscript{6} symmetry while remaining 2/3\textsuperscript{rd} of atoms occupies C\textsubscript{2} symmetry [42]. The optical transitions in Eu\textsuperscript{3+} states are more likely to occur in the C\textsubscript{2} site rather than in S\textsubscript{6} site due to its more stable inversion symmetry of the lattice [42]. Therefore only certain magnetic dipole transitions are allowed in the S\textsubscript{6} sites, while the electric dipole transitions are preferred in C\textsubscript{2} sites. More over S\textsubscript{6} site are less in number which will reduce the intensity of PL emission of magnetic dipole transitions [59].

In the observed emission spectra, the lines at 538-585 nm (\textsuperscript{5}D\textsubscript{1} - \textsuperscript{7}F\textsubscript{1}) corresponds to magnetic dipole transitions while that at 590-715 nm (\textsuperscript{5}D\textsubscript{0} - \textsuperscript{7}F\textsubscript{j}, j = 0 to 4) corresponds to electric dipole transitions which include emission peak at 615 nm. In the observed spectra the relative intensity of magnetic dipole transitions are less compared to that of electric dipole transitions. Here, from the PL spectra it is concluded that Eu\textsuperscript{3+} ions are incorporated in to the host lattice and most of the ions predominantly replace yttrium ions with C\textsubscript{2} symmetry.
The PLE spectra (figure 4.28) shows clearly distinct bands, one corresponding to band to band excitation of the host (212 nm) and the charge transfer band (245 nm). These excitations correspond to the peak emission wavelength at 615 nm, intensity maximum being observed for charge transfer band and resonant transfer takes place from CT states. The PLE also exhibits the high crystalline quality of the deposited films.

Figure 4.28. PLEexcitation spectra \( Y_2O_3:Eu \) thin films deposited at 700°C and 10\(^{-4}\) mbar \( PO_2 \). (\( \lambda_{em} = 615 \) nm)
4C.3.4 The CIE coordinates

Figure 4.29. CIE chromaticity diagram of the $\text{Y}_2\text{O}_3$:Eu thin films deposited at various substrate temperature.

The CIE coordinates of the deposited films lie in the yellowish-orange range of the coordinate diagram (figure 4.29). It is observed that as temperature increases the coordinates shift to red region of the diagram. The coordinates of the film that showed maximum PL intensity are $(x,y) = (0.52, 0.47)$. 
Conclusion

Eu doped Y$_2$O$_3$ thin films were deposited on amorphous fused silica substrates using pulsed laser ablation technique. The effect of oxygen partial pressure (PO$_2$) and substrate temperature on the structural and optical characteristics of the deposited films were investigated. All the deposited films were crystalline, irrespective of oxygen partial pressure and substrate temperature used for deposition. Film deposited at 0.05 mbar PO$_2$ showed better crystallinity with minimum FWHM at a substrate temperature of 600°C. All the films deposited at various substrate temperatures and different partial pressure (at 600°C) exhibited red luminescence peaking at 615 nm corresponding to $^5$D$_0$-$^7$F$_1$ transition in Eu$^{3+}$. PLE spectra exhibited two bands one corresponding to band to band excitation (212 nm) of the host and other to charge transfer band excitation (245 nm).

References


61. JCPDS card no: 11-0687
62. JCPDS card no: 36-1479