CHAPTER 1

An Introduction to Electroluminescence and Oxide Phosphors
This chapter gives an introduction about the device structure, mechanism of electroluminescence and materials used in alternating current thin film electroluminescent (ACTFEL) devices. A general review on oxide phosphors particularly ZnGa$_2$O$_4$, Zn$_2$GeO$_4$ and Y$_2$O$_3$ is also given in this chapter.
ac thin film EL (ACTFEL), ac powder EL (ACPEL), dc thin film EL and dc powder EL. DCEL has been widely used for small displays on glass in automobiles usually as yellow fixed messages and for backlighting purposes. AC electroluminescence has opened up a whole new world, however. Figure 1.1 outlines some comparative remarks on the four kinds of EL devices. ZnS:Mn based ACTFEL displays of laptop personal computers and word processors and ACPEL backlights for liquid crystal displays are today commercially available. Powder EL displays have virtually unlimited potential, i.e., uniform light emission, thin profile and low power consumption [1]. Flexible powder EL devices can be made on polyethylene terephthalate (PET) coated indium tin oxide (ITO) substrates [2, 3]. Powder EL lights have been used for architectural and decorative lighting and as LCD backlights in cellular phones, personal digital assistants (PDA) and palmtop computers. But they also possess multiplexing limitations and suffer from low luminance, high operating voltage, poor contrast and significant luminance degradation over fairly short time (~ 500 hours). With the development of thin-film process technology in the 1960's, the initial efforts to utilize the phenomenon of electroluminescence on powder EL devices helped in developing thin-film EL devices.

Thin film phosphors have several advantages in comparison to the powders, such as higher lateral resolution from smaller grains, better thermal stability, reduced out-gassing, and better adhesion to the solid surface [4]. However, the biggest drawback in the use of phosphor thin films is their low brightness and efficiencies in comparison to those of bulk powder materials which are primarily associated with factors such as internal reflection, the small
interaction volume between incident beam and solid and absorption of generated light by substrate materials.

![Diagram of A C Drive and D C Drive](image)

**Figure 1.1 Comparison between the four types of EL displays**

The ACTFEL displays have emerged as the most dependable emissive display technology owing to its unique features are explained below.

**Solid-state nature:** Fundamental to an EL device is its solid state construction which enables it to be fully integrated onto the substrate of the drive electronics. The solid-state nature makes them extremely rugged, a characteristic desirable for an FPD used in portable applications and harsh environments. The solid state construction makes it more resistant to shocks and vibrations. The luminous emission in a solid-state environment eliminates the risks involved in maintaining a vacuum or plasma environment, as in the case of VFDs, PDPs or FEDs.

**Ruggedness:** These solid-state devices are insensitive to shocks and wide temperature variation. They can, therefore, withstand aggressive environments - cold, heat, wind, dust, vibration, sunlight. So TFEL displays are very apt to be used in military equipments and spacecrafts.
Wide viewing angle: The emissive EL displays offer a viewing angle greater than 160° which is an inherent problem with the LCD displays. The absence of optical elements in the light path (other than the glass substrate) renders them this property and so very useful for medical and industrial applications.

Wide operating temperature: EL panels can be operated over a wide temperature range of –25°C to 60°C (limited by the drive electronics) and therefore can serve in many critical military and industrial applications. They don't freeze or get slow or dim even at low temperatures.

Long life: The panel itself has no significant wear-out mechanism. Display panels have demonstrated device lifetimes of over 50,000 hours with less than 10% luminance change.

High contrast: This property gives EL displays what we call "at a glance" readability. This property makes them highly efficient in a very high ambient illumination environment such as in industrial instrumentation.

Better display qualities: Fast response, high resolution and small pixel size are some of the best qualities of an EL display. They operate at video rates high enough to produce high information content FPDs with the image quality of the CRT.

1.2 Electroluminescence

Electroluminescence is a non-thermal generation of light resulting from the application of an electric field to a substance. The effect was first discovered by G. Destrieu in 1936 in ZnS, when a large electric field was applied to it. There are two classes of EL devices. One is Light emitting diodes (LEDs) where light is generated by electron-hole pair recombination at a p-n junction which is also
known as injection luminescence while in high field EL, light is generated by impact excitation of a luminescent center (also called activator) by high energy electrons. Typical electric field through which electrons are accelerated is nearly $10^6$ V/cm. So this type of luminescence is also referred as high field luminescence. Based on this high field luminance there are four types of EL devices namely ac thin film EL, ac powder EL, dc thin film EL and dc powder EL. They are categorized on the basis of drive voltage and the phosphor configuration. Since the thesis is focused on ac thin film EL devices, the structure and physics of ACTFEL devices are discussed in detail.

### 1.3 EL device Structure

There are three general configurations for thin film EL device structures. One is conventional standard structure that comprises of Metal–insulator–semiconductor-insulator-metal (MISIM) structure [fig. 1.2(a)]. Second one is an inverted type structure [fig. 1.2(b)] and in third one usually one insulator normally a thick dielectric/ceramic [fig. 1.2(c)] is used. In the standard structure phosphor layer is sandwiched between two insulators (dielectric). Here bottom electrode which is transparent (usually ITO) while top electrode is opaque (usually Al/Au/In). In the inverted structure, the electrodes are simply inverted so that no light emission will take place in the opposite direction through the substrate unlike that in standard case. The advantage is that we can use non-transparent substrates like silicon which could withstand higher temperatures. In the standard structure, normally glass substrates are used and it will not withstand high processing temperatures.
Some researchers employ the structure shown in figure 1.2(c) which consists of only single insulator that acts as substrate/insulator. The thickness of this ceramic insulator/substrate will be 0.2mm while that of other layers will be in nm/μm regime. The bottom opaque electrode will be deposited on the back side of the dielectric sheet and top electrode will be transparent and light emits through this electrode. Here we have an advantage that the structure is simple and higher post deposition annealing temperatures (1100°C) could be employed to improve the crystalline quality of the phosphor layer which is not possible in the case of glass substrates.

1.4 Ideal ACTFEL device

The basic ACTFEL device structure can be modeled as a simple circuit where the insulators are represented by perfect capacitors and the phosphor layer is represented by a capacitor below the threshold voltage and a pair of back-to-
back diodes above threshold voltage [5]. The equivalent-circuit model shown in figure 1.3 very well demonstrates the essential phenomenological physics of a thin-film EL device.

Figure 1.3 (a) Equivalent circuit of an ideal ACTFEL device and (b) Ideal I-V characteristics of the non-linear resistor of the phosphor layer

Below the threshold voltage, the model treats the TFEL device as a three series capacitor circuit where the voltage drop across each layer is proportional to the dielectric constant and the layer thickness. The first and second insulating layers are incorporated into one effective insulating layer with the effective capacitance per unit area, $C_I$, given by

$$C_I = \frac{C_{11}C_{12}}{C_{11} + C_{12}}$$

(1.1)

where $C_{11}$ and $C_{12}$ are capacitances per unit area of the first and second insulating layers, respectively. The thin-film phosphor also behaves as a capacitor below the threshold voltage $V_{th}$ with the capacitance per unit area $CEL$. However, above the threshold voltage real (dissipative) current flows in the phosphor layer and gives rise to the light emission. Therefore, the phosphor layer is described as a capacitor in parallel with a non-linear resistor with the I-V
characteristic shown in figure 1.3(b). In an ideal case, this non-linear resistor can be simulated by back-to-back Zener diodes. The dependence of the device performance such as transferred charge density, power dissipation and luminance are expressed in terms of device parameters such as layer thickness, dielectric constant, dielectric breakdown strength, threshold field and luminous efficiency.

Voltage applied across the device,

\[ V_a = V_I + V_{EL} \]  \hspace{1cm} (1.2)

where \( V_I \) and \( V_{EL} \) represents the voltage across the insulating layers and the phosphor layer respectively. Now apply a pulse \( P1 \) whose magnitude is less than the threshold voltage. Below \( V_{th} \), \( V_a \) is capacitively divided. When \( V_a \) exceeds \( V_{th} \), the resistive branch turns on and current flows (with accompanying light emission) to discharge the voltage across the phosphor capacitor back to the threshold level. After electron injection begins in an ideal device, all of the additional externally applied voltage is dropped across the dielectric layer(s) and the phosphor layer voltage remains constant. So the resistive branch must supply current to charge up the insulating layer capacitor by an equal voltage.

1.5 The EL Mechanism

The basic mechanism of electroluminescence as in the case of double insulator structure (standard) is discussed below. As we are discussing about AC-TFEL device, there are many waveforms like sine, triangular, trapezoidal, square that are generally used for exciting the devices. The usual convention is to refer the applied voltage to bottom electrode so that positive voltage is applied to Al (opaque) electrode. Since phosphor and insulator are wide band gap
semiconductors, we assume that there are no free charge carriers when the device is operated below threshold and it looks like a simple capacitor. The applied voltage is dropped in the dielectric and phosphor layer due to their capacitance. When the applied voltage reaches threshold voltage the device no longer behaves like a capacitor as the field in the phosphor increases and charge will start flowing through the device. Beyond the threshold voltage the device operation can be simply visualized as in the energy band diagram shown in the figure 1.4. Due to the disorder encountered on an atomic scale at the insulator-phosphor interface, large number of allowed electronic states is present within the phosphor band gap at the interface. Ideally these states can be regarded as single discrete trap level with a large occupancy of electrons. When the phosphor field exceeds a particular threshold, these trapped electrons at the interface level begin to tunnel emit into the phosphor conduction band as shown in the process (1) in the figure. Due to large electric field experienced by these electrons when they enter the phosphor conduction band, these electrons will drift across the phosphor layer (process 2). As electrons moves, in the diagram it is shown farther and farther higher in energy from the conduction band, showing that electron is gaining kinetic energy from the electric field. As it traverse the phosphor field, an electron may randomly collide with the atoms in the lattice, losing energy in the process, before again gaining the energy from the field. If a sufficiently energetic electron (energy for exciting the luminescent center) collides with a luminescent impurity, which is then excited in to higher energy state (process 3). The electron will continue traversing the phosphor layer due to the presence of electric field until it reaches the conduction band discontinuity between the phosphor and dielectric layers at the anodic side of the device. Here
it thermalizes, releasing heat energy to the lattice, to the bottom of conduction band and is re-trapped in a deep level at the interface states at phosphor-dielectric interface at anodic side (process 4). In the mean time the excited electron in the luminescent center will relax back to ground state (process 5) eventually emitting a photon, provided the transition is radiative. This photon is out-coupled from the device (process 6) through the transparent contact. When the applied voltage reaches maximum value in temporal scale, electron emission rapidly ceases. As electrons are emitted from the cathodic interface and drifted across the phosphor layer reaches the anodic interface, a net positive charge is left at the cathodic interface and a net negative charge adds to the anodic interface thereby introducing a polarization charge effect. This polarization field has some effects on the device operation. It can act as a negative feed back mechanism which makes it difficult to inject more electrons from the cathode. If a high density of electrons are available at the interface discrete trap level, they are injected fast enough that, even while the external voltage is increasing, the phosphor field remains at a steady state value or we can say that after electron injection begins, all the additional voltage applied to the device will drop across the dielectric layers keeping the phosphor layer voltage /field a constant. Other effect of polarization charge when the applied voltage reaches a zero value, this polarization field becomes prominent. This field causes the electrons that are trapped at the anodic side to re-emit in to the phosphor layer. This charge is mentioned as leakage charge. Moreover when the following negative pulse is applied to the device the external field is augmented by the polarization field which reduces the phosphor threshold at a lower external applied voltage than the threshold, termed as turn on voltage. Additionally, electrons begin to tunnel
at a lower external voltage and trap occupancy is larger and more charge is transferred across the device than during the previous one.

Figure 1.4 Energy band diagram of ACTFEL device

This establishes a larger polarization field so that turn on voltage is further reduced and the transferred charge amplification repeats. This process will continue till a steady state operating condition is established. In an ideal phosphor system, steady state operation may be established after only a few cycles.

1.6 Space charge in EL devices

One of the major deviations from the ideal operation of ACTFEL devices is the formation of space charge within the phosphor layer. "Space" in
the ACTFEL context refers to positive space charge and can arise in a number of ways. First and foremost reason is, with in the phosphor region, traps may be ionized via thermal or field emission or as a result of electron impingement. The removed electron is swept away by the electric field as the electrons experience a high field in the phosphor layer. Now the trap is positively charged and therefore acts to bend the energy band locally downwards. The ionized center may be intentionally added impurity which could act as a donor due to valency mismatch or a luminescent impurity whose excited states lie close to conduction band or a vacancy or a point defect. Another common source of space charge is band to band impact ionization of the lattice. Along with the band to band impact ionization, a hole is also left or created in the valence band while an electron is promoted to the conduction band as a delocalized charge carrier. This hole may drift towards the cathode a short distance before it is trapped resulting in a localized positive charge which will pull the band downward. The space charge induced curvature of band under device bias is shown in the figure 1.5. The dotted lines show the spatial dependence of the phosphor layer energy band locations in the absence of space charge. The linearity of band is indicative of the fact that a uniform electric field exists throughout the phosphor. The effect of space charge is bending of the band represented by curved lines. Compared to a phosphor layer with no space charge, electric field near cathode is greater for a phosphor layer with space charge, even though the externally applied potential is same in both cases, since the tunnel emission rate of electrons is a strong function of electric field. On the contrary electric field near anode will be reduced due to lesser field experienced due to the presence of space charge. This results in lesser density of energetic electrons in this region, which reduces
the probability of impact excitation. But it creates hot electron induced damage at the anodic phosphor-insulator interface. The lower electric field at the anodic region may lead to efficient carrier trapping, which is not appreciable at the high field cathodic region. Depending on the mechanism of space charge creation and light emission in a particular phosphor system, this will have noticeable effect in device operation.

![Figure 1.5 Space-charge induced band bending of phosphor layer in ACTFEL device](image)

Space charge in ACTFEL devices can be classified in to either static or dynamic depending on the nature of spatio-temporal distribution. Normally the space charge created will be annihilated at some characteristic rate. The annihilation may be due to recombination of an electron with an ionized trap or the re-emission of trapped hole. If the annihilation proceeds at a slow rate,
compared to ac drive waveform, the space charge forms a steady-state distribution and is denoted as static. Dynamic space is that portion of total space charge that is not in steady state but both created and annihilated within one period of the drive waveform.

All well known ACTFEL phosphor systems have been found to exhibit space charge effects. The presence of space charge reduces the voltage necessary for drive operation which will in turn improve reliability and efficiency. On the other hand, if the space charge is dynamic, the energy expended creating and maintaining the space charge may reduce efficiency.

1.7 ACTFEL Materials

The materials that are used in ACTFEL devices are

1.7.1 Substrate

For a standard device, the primary requirements for the substrates are transparency, smooth surface, ability to withstand thermal treatments and the material should be inexpensive in a commercial viewpoint. Therefore most commonly used substrate is glass. In the present study, the devices were fabricated on ITO/ATO coated ohara and NEG glass was supplied by Planar Inc., U.S.A.

1.7.2 Electrodes

There are two types of electrodes used in standard structure, one is transparent through which light is viewed and other is opaque.
(a) Transparent electrode

The transparent electrode should be sufficiently conducting, transparent in the entire visible region of the electromagnetic spectra and it should withstand higher thermal processing of subsequent layers. The most commonly used material is indium tin oxide (ITO). A thickness of 200 nm is generally used. Another material that is used as transparent electrode in ACTFEL device is ZnO:Al. In the present study ITO is used as transparent electrode.

(b) Opaque electrode

The critical requirements for opaque electrode in a standard device structure are it should be highly conducting, good adhesion to the top insulator. Al is most commonly used electrode, and also in this study. The advantages of Al are, it is inexpensive, can be easily deposited using thermal evaporation, it has low melting point which enhances the possibility for self-healing breakdown fusing of metal surrounding the short. Typically the thickness of the electrode lies in 100-200 nm range.

1.7.3 Insulators

The insulating layers of are important layers of the device structure. The insulator undergoes same thermal processing as the phosphor layer and therefore must have good thermal stability and chemical compatibility with the bottom electrode. The critical requirements of insulator layers are

1. High dielectric constant, $\varepsilon_0\varepsilon_r$
2. High dielectric breakdown electric field, $F_{BD}$
3. Small number of pinholes and defects
4. Good adhesion
5. Small loss factor, $\tan \delta$

In order to maximize the voltage drop across the device, the capacitance of the phosphor layer should be low as compared to insulators. The capacitance of the layers is calculated as

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

Where $\varepsilon_0 \varepsilon_r$ is the dielectric constant of the insulator material, $A$ is the area of cross-section and $d$ is the thickness of the insulator layer. Therefore to optimize/maximize the insulator capacitance the dielectric constant should be high and the thickness layer should decrease. It is also logical to reduce the layer thickness instead of selecting high dielectric constant material. However, there is a lower limit to thickness, as defects and pinholes will be high, if the thickness is low. Moreover, the breakdown field strength is inversely proportional to the thickness of the layer ($E = V/d$). Therefore, thinner layers will have higher electric field.

It is generally observed that materials with higher dielectric constant have a small breakdown strength and vice-versa. Furthermore, the high dielectric constant material tends to exhibit propagating breakdown. The dielectric materials used in this study are ATO, which is a stack of $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ and BTO ($\text{BaTa}_2\text{O}_6$). The ATO layer was deposited by Atomic layer epitaxy method (ALE) by Planar Inc. In the present study, the top insulator BTO was deposited using rf magnetron sputtering.

### 1.7.4 Phosphor layer

The phosphor layer also called active layer typically comprises of a host and an activator/luminescent center. The host by its definition is the material/environment for activator or luminescent center which converts input
energy in to visible light. Generally sulphides are used as host materials in the ACTFEL devices. However oxides, due to its inherent advantages over sulphides, are also used as hosts for ACTFEL devices. The requirements for a phosphor host that are used in ACTFEL devices are

1. The host bandgap must be large enough not to absorb any emission from the luminescent center. For complete visible transmission, this requires a band gap of at least 3.1eV.

2. The host must be a good insulator below threshold. This is required to maintain a voltage drop and subsequent electric field across the phosphor layer, leading to the sub-threshold capacitive nature of the phosphor.

3. The host must have high breakdown strength to allow for efficient acceleration of electrons. This requires that the breakdown field of the phosphor must be at least 1MV/cm.

4. The host must have good crystallinity and a low phonon-coupling coefficient to minimize electron scattering.

5. Must be able to withstand the requisite post annealing treatments.

The emission of a phosphor is determined by activator/luminescent center. In addition, the host lattice influences the color emitted by an activator, since different hosts provide different crystal field environment for these activators. In the case of transition metals ($\text{Mn}^{2+}$, $\text{Cr}^{3+}$, $\text{Ag}^{+}$, $\text{Cu}^{+}$, $\text{Ti}^{4+}$ etc) that are used as activators, the emitted light is highly influenced by the crystal field environment as outer d shell is involved in the emission process. But in the case of rare earth ions ($\text{Eu}^{3+}$, $\text{Dy}^{3+}$, $\text{Tm}^{3+}$, $\text{Tb}^{3+}$, $\text{Ce}^{3+}$) that are used as activators, the emitted light is not much influenced by the crystal field environment, because
inner f shell is involved in the light emission process. The requirements of a luminescent material for suitable application in TFEL devices are

1. should be properly incorporated into host material and emit visible light
2. should have a large cross section for impact excitation
3. Stable in the high electric field (>10^6 V/cm).

In the present work oxide phosphor hosts like ZnGa2O4, Zn2GeO4, Mg2GeO4 and Y2O3 are studied and activators used are Mn^{2+} and Eu^{3+}.

1.8 Oxide Phosphors

In the early 1990s oxide phosphors were introduced as a substitute to commercially available and well established phosphor class namely sulphides. Due to their inherent disadvantages like lack of primary color emission, instability in vacuum, inferior chemical, mechanical and thermal stability, corrosive gas emission under electron bombardment, it became a necessity to find a substitute that could satisfy the requirements of the display industry. So researchers around the world started working on another class of phosphors namely-oxide phosphors. Several binaries, ternaries and complex oxide phosphors were proposed and still continue proposing. ZnO, is such a binary oxide is also used a phosphor by doping with Mn.

First report of high luminance oxide phosphor TFEL device using Zn2SiO4:Mn, a ternary compound host material came in the early 1990s [6]. After that high luminance red and green emissions were realized using Mn/Eu doped oxide hosts [7, 8]. The table shows emission colour of certain oxide phosphors.

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Table 1.1 Emission colour of certain oxide phosphors

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Color</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$_3$(PO$_4$)$_2$:Eu</td>
<td>Blue-Violet</td>
<td>9</td>
</tr>
<tr>
<td>Ba$_3$(PO$_4$)$_2$:Ti</td>
<td>Blue-Violet</td>
<td>9</td>
</tr>
<tr>
<td>ZnGa$_2$O$_4$</td>
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<td>10</td>
</tr>
<tr>
<td>ZnGa$_2$O$_4$:Ce$^{3+}$</td>
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<td>11</td>
</tr>
<tr>
<td>Y$_2$SiO$_5$:Ce$^{3+}$</td>
<td>Blue</td>
<td>12</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$: Tm$^{3+}$</td>
<td>Blue</td>
<td>12</td>
</tr>
<tr>
<td>LaAlGe$_2$O$_7$:Tm</td>
<td>Blue</td>
<td>13</td>
</tr>
<tr>
<td>BaMgAl$<em>{10}$O$</em>{16}$:Eu$^{2+}$</td>
<td>Blue</td>
<td>12</td>
</tr>
<tr>
<td>TaZn$_3$O$_8$</td>
<td>Blue</td>
<td>14</td>
</tr>
<tr>
<td>Ga$_2$O$_3$:Mn$^{2+}$</td>
<td>Green</td>
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</tr>
<tr>
<td>ZnGa$_2$O$_4$:Mn$^{2+}$</td>
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<tr>
<td>ZnGa$_2$O$_4$:Tb$^{3+}$</td>
<td>Green</td>
<td>15</td>
</tr>
<tr>
<td>Zn$_2$GeO$_4$:Mn$^{2+}$</td>
<td>Green</td>
<td>16</td>
</tr>
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<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$: Eu$^{3+}$</td>
<td>Red</td>
<td>12</td>
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</table>
### 1.9 Zinc gallium oxide- ZnGa$_2$O$_4$

Zinc gallate or Zinc gallium oxide is a ternary oxide phosphor which has been proved as an efficient host material for electroluminescent devices.

ZnGa$_2$O$_4$ is a low voltage cathodoluminescent (LVCL) phosphor. Itoh et al. has utilized this property in realizing vacuum fluorescent displays [10]. ZnGa$_2$O$_4$ does not cause damage to filaments in VFDs, unlike conventional sulfide phosphors. Blue luminescence at 470 nm and a chromaticity at $X = 0.170$ and $Y = 0.130$ was observed from the bulk phosphors prepared at various firing
temperatures. A luminous efficiency of 0.7 lm/W has been obtained, when the VFD with this phosphor is operated at 30 V dc and the device shows excellent stability [10]. Since ZnGa$_2$O$_4$ has a wide band gap, it has been investigated as a UV-transparent electronic conductor [36].

Doped and undoped ZnGa$_2$O$_4$ bulk phosphor has been prepared using various preparation techniques like solid state reaction [36-48], oxalate gel synthesis [49], sol-gel route [50], aerosol pyrolysis [51], citrate gel process[52], microencapsulation method [53], multi-stage precipitation method [55]. Omata et al. has investigated ZnGa$_2$O$_4$ phosphor for possible application in uv-transparent conducting oxide [36]. In solid state reaction using the mixture of ZnO and Ga$_2$O$_3$ in 1:1 molar ratio, single phase of ZnGa$_2$O$_4$ has been formed when the mixture was fired at and above 1000°C for 24 hrs [39]. From the XPS analysis, the separation between the Zn $^2p_{3/2}$ and Ga $^2p_{3/2}$ peaks, can be used as a sensitive tool to distinguish between a complete formation of ZnGa$_2$O$_4$ compound and a mixture of ZnO and Ga$_2$O$_3$ powders [39].

1.9.1 Crystal Structure

ZnGa$_2$O$_4$ with formulae AB$_2$O$_4$ has a cubic-spinel structure which can be viewed as a combination of rock salt and zinc blende structures. It has a close packed cubic arrangement of anions with one half of the octahedral holes and one eighth of tetrahedral holes filled with cations (fig.1.6). If A$^{2+}$ are in tetrahedral sites and B$^{3+}$ are at octahedral sites, we call the spinel as normal spinel. If A$^{2+}$ are at octahedral sites and half of the B$^{3+}$ are at tetrahedral and the other half at octahedral sites, then it is called inverse spinel structure. The distribution of cations can be intermediate which is known as mixed spinel structure. The ZnGa$_2$O$_4$ is found to be a normal spinel with all Zn$^{2+}$ ions at
tetrahedral sites and $\text{Ga}^{3+}$ at octahedral sites with lattice constant $a = 8.37$ Å. The oxygen ions are in the face centered cubic closed packing. For a sub cell of this structure, there are four atoms, four tetrahedral interstices and eight octahedral interstices. This makes a total of twelve interstices to be filled up with three cations, one divalent and other two trivalent.

Figure 1.6 The spinel structure of ZnGa$_2$O$_4$

In each elementary cell two octahedral sites are filled and one is tetrahedral. Eight of these elementary cells are arranged so as to form a unit cell containing 32 oxygen ions, 16 octahedral cations and 8 tetrahedral cations.

The optical band gap of ZnGa$_2$O$_4$ is found to be 4.4 eV which is a direct band gap.

1.9.2 Photoluminescence

ZnGa$_2$O$_4$ exhibits strong blue luminescence due to transition via self activated center on excitation with ultraviolet light or low energy electrons.
ZnGa$_2$O$_4$ doped with Mn or Cr exhibits green or red luminescence. In ZnGa$_2$O$_4$, Ga acts as sensitizer. The effect of excess Ga$^{3+}$ ions is proposed just like Cr$^{3+}$ ions in the spinel structure [41]. The wave functions of the S,P,D... terms are similar to those s,p,d,... orbitals, because the terms differ slightly from those of the corresponding orbitals, and so they may transform differently in a particular point group. For example, in the octahedral structure, p orbitals transform as $T_{1u}$, the P term which is derived from the d configuration transforms as $T_{1g}$. Because of the interactions, the orbitals of the transformed p term with the orbitals of the six oxygen ligands, result in shifts in the energy levels of the individual orbitals resulting in the splitting of the 3d energy levels occurs and degeneracy is lifted. The most commonly observed octahedral or tetrahedral environments lead to different arrangements. The effect of the strength of ligand field in an octahedral environment on the resultant energy levels, labelled by their spectroscopic terms $^{4}A_2$, $^{4}T_1$, $^{4}T_2$ and $^{2}E$ are shown in the figure 1.7.

![Ga$^{3+}$ level splitting in an octahedral environment](image-url)

Figure 1.7 Ga$^{3+}$ level splitting in an octahedral environment
A broad fluorescence band peaking at 432 nm is observed when excited with UV light of 260 nm. This luminescence originates from self activated Ga at octahedral site. Jeong et al. [41] investigated compositional dependence of the luminescence of zinc gallate prepared by solid state reaction technique, firing at 1250°C for 4 hrs. They prepared phosphors with nominal formulae $\text{ZnGa}_x\text{O}_{1+1.5x}$ with $x$ (Ga/Zn ratio) varying from 1.98 to 3. They observed a broad emission band peaking at 432 nm, for the excitation band peak at 260 nm. The intensity of the band increases continuously as Ga/Zn ratio increases from 1.98 to 2.02. This increase in intensity was attributed to the increase in oxygen vacancy due to excess Ga$_2$O$_3$. When Ga/Zn ratio was above 2.03, the excitation and emission were very different from those of stoichiometric ZnGa$_2$O$_4$. A shoulder peak at 246 nm was developed with decrease in intensity of excitation peak at 260 nm. The emission wavelength shifted to 360 nm. This peak cannot be considered to be originated from $\beta$-Ga$_2$O$_3$ even though the excitation and emission spectra of $\beta$-Ga$_2$O$_3$ heat treated at same conditions showed similar behaviour. Most spinels show a solid solution with B$_2$O$_3$ type oxides, hence solubility of Ga$_2$O$_3$ in the ZnGa$_2$O$_4$ lattice is expected. Therefore the absorption band peaking at 260 nm and emission at 432 nm corresponds to transition in octahedral Ga-O groups in the spinel lattice. The absorption and fluorescence at 246 nm and 360 nm can be related with self activated optical centers due to the tetrahedral Ga-O group. Randomness of the spinel structure having the formulae $(A_{1-x}B_x)^{IV}(B_{2-x}A_x)^{VI}O_4$ is also reported and this randomness is not necessarily a constant. In some cases this randomness can be varied by appropriate heat treatment.

The randomness of the spinel structure can be determined by X-ray diffraction and neutron diffraction. If there is a sufficient difference between the
X-ray scattering powers of Zn and Ga, it might have been possible to determine the distribution of these atoms by the usual methods of X-ray crystallography. In ZnGa$_2$O$_4$ the scattering powers of Zn and Ga, are almost the same. Another possibility is to distinguish from IR spectra. In the IR spectrum of zinc gallate, vibration peaks appear at 420 cm$^{-1}$ and 570 cm$^{-1}$. However, to differentiate the peak of the tetrahedral Ga-O from that of the octahedral Ga-O was difficult. Even though it is not possible to identify the Ga site neither by XRD nor by IR spectroscopy, Ga$^{3+}$ ions be not only on the octahedral sites but also on the tetrahedral sites when the zinc gallate is synthesized with β-Ga$_2$O$_3$ under the gallate rich environment. Therefore, the excitation band at shorter wavelength (peaking at 246 nm) and the fluorescence band at 360 nm is considered to originate from the gallium at the tetrahedral sites when excess gallium is introduced in the spinel. Moreover color tuning has been observed via oxidation or reduction process of ZnGa$_2$O$_4$ phosphor. The color oscillates between ultraviolet (360 nm) and blue (430 nm). The ultraviolet emission of reduced ZnGa$_2$O$_4$ always accompanies 680 nm emission originating from single oxygen vacancies ($V_{0^*}$). They observed an increase in the difference in binding energy between Ga$^{3+}$ and O$^{2+}$ in reduced ZnGa$_2$O$_4$ indicates that the configuration of octahedral sites is distorted due to $V_{0^*}$ generation and it becomes more ionic which shifts the emission band from 430 to 360 nm.

ZnGa$_2$O$_4$ exhibits green emission on doping Mn$^{2+}$ ions. The excitation energy of zinc gallate is transferred in a non-radiative manner from the host lattice, Ga-O group acts as sensitizer to Mn$^{2+}$ center. In order to get green emission of good color and purity, ZnGa$_2$O$_4$:Mn phosphor has to be annealed in a reducing atmosphere to convert Mn$^{4+}$/Mn$^{3+}$ to Mn$^{2+}$. Interestingly during this
annealing process in a reducing atmosphere, not only reduction of Mn ions will take place but also redistribution of Ga ions in the spinel structure will occur. As the spectral overlap of and is large, the transfer will occur in a non-radiative way from Mn$^{2+}$ to Mn$^{3+}$ reducing the luminance output. Yu and Lin reported a weak red emission at 666 nm when excited at 325 nm [37]. The green emission at 508 nm is observed which can be attributed to $^{4}T_{1}$$-^{6}A_{1}$ transitions of tetrahedrally coordinated Mn ions. The PLE of the phosphor when monitored at 508 nm was observed at 245 nm and 290 nm. The band at 245 nm is the direct excitation of the host, in particular the Ga-O group and that at 290 nm corresponds to direct excitation or the charge transfer band of the Mn$^{2+}$ ions. Shea et al. [55] observed the green emission at 506 nm while Tran et al. [56] measured this luminance at 503 nm. Moreover Tran et al. reported that the emission at lower temperature can be attributed to three emission centers 1) Mn at tetrahedral Zn site, 2) at Zn$^{2+}$ site with distorted tetrahedron and 3) Mn at octahedral Ga$^{3+}$ site [56]. But Poort et al. reported emission from only one centre which is Mn$^{2+}$ at Zn$^{2+}$ site [57]. They calculated the effective distance of energy transport as 40 Å at 4.2 K. Uheda et al. suggested that the long term phosphorescence of ZnGa$_2$O$_4$:Mn is due to the formation of several trap states, mainly due to Zn vacancies [38]. These trap states lie in the energy range 0.48-0.71 eV above the valence band of the host. Several authors had reported enhancement in luminous intensity via co-doping the phosphor with other impurities. For example 5% enhancement in luminous intensity has been observed for Ge and Li codoped ZnGa$_2$O$_4$:Mn phosphor. Cd codoping has resulted in red-shift of emission wavelength in ZnGa$_2$O$_4$:Mn bulk phosphor due to effective change in crystal field. Choi et al. observed that the solid solubility limit of Cd in bulk ZnGa$_2$O$_4$ phosphor is 0.6
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and a red shift of emission wavelength from 350 to 520 is observed [40]. The PL and CL emission intensity were found to increase with In$_2$O$_3$ doping also [41].

Thin films of doped and undoped ZnGa$_2$O$_4$ has been deposited on various amorphous and single crystalline substrates using physical vapour deposition techniques like pulsed laser deposition [58-70], rf magnetron sputtering [71-82], solvent evaporation [83], sol-gel process [84] and electrophoretic deposition [86]. Thin films were deposited using pulsed laser deposition on various substrates including single crystalline substrates like Al$_2$O$_3$, MgO and Si. The effect of Se doping on luminescent characteristics of ZnGa$_2$O$_4$:Mn phosphor thin films deposited on MgO substrates were studied by Jeong et al. and they found that MgO is one of the promising substrates to grow highly crystalline thin films of ZnGa$_2$O$_4$ [62]. The brightness of the phosphor was found to increase by a factor of 3.1 compared to as deposited phosphor without Se [62]. Bae et al. [63] reported that Al$_2$O$_3$ (sapphire) is also one of the most promising substrate to grow high quality thin films compared to Si. An increase in β-Ga$_2$O$_3$ phase is observed as the annealing temperature was 600°C and above [63]. Epitaxial thin films of ZnGa$_2$O$_4$:Mn has also been deposited on MgO substrates using pulsed laser ablation and the effect of Zn/Ga ratio on crystalline luminescence were studied and a Zn/Ga ratio of 0.4 resulted in bluish-white light [64]. PLD has been used for growing high crystalline quality epitaxial thin films, rf magnetron sputtering has been used by several authors to deposit polycrystalline thin films of doped and undoped ZnGa$_2$O$_4$. Hseih et al. has observed low voltage cathodoluminescence from rf magnetron sputtered ZnGa$_2$O$_4$ thin film and the effect of substrate temperature and annealing temperature were studied [70]. Chung et al. has studied the effect of annealing of
sputtered ZnGa$_2$O$_4$ grown on various substrates like ZnO:Al/glass, ZnO:Ga/glass, ZnO/ITO/glass and ITO/glass. The surface morphology and luminescent properties of thin films depend on the crystallinity of the substrates. But the annealing conditions didn’t affect the surface morphology while luminescent characteristics and Zn/Ga ratio were susceptible to annealing conditions [71]. The sputtered ZnGa$_2$O$_4$ on Si substrate resulted in lower grain size film and higher PL intensity than grown on ITO/glass substrate [73]. Better crystalline films were obtained when ZnGa$_2$O$_4$ was deposited over In$_2$O$_3$ buffer layer and a white luminescence is observed from the films [75]. The microstructural characteristics of thin film ZnGa$_2$O$_4$ :Mn phosphors grown by rf planar magnetron sputter deposition has been investigated by Kim et al.. The energetic particle bombardment has been found to have dramatic effects on the cross-sectional microstructure, degree of porosity, surface morphology, and film density of the deposited thin films [76, 77]. The ZnGa$_2$O$_4$ thin films deposited at 600°C were found to show better luminescence while post deposition annealing improves the PL and CL performance of the phosphor.

ZnGa$_2$O$_4$ has been demonstrated as an excellent host material for multicolor-emitting phosphor layers in ACTFEL devices. Minami et al. has fabricated Mn, Cr, Ce, doped ZnGa$_2$O$_4$ ACTFEL devices using the single insulating layered structure [11]. The phosphor layers were sputter deposited onto 0.2 mm thick ceramic sheets of BaTiO$_3$. ZnO:Al/ITO and Al/Ag were used as top and bottom electrodes respectively. The as-deposited devices were post-annealed at 1020°C for 5 hrs in argon ambient [11, 85, 86] or subjected to in-situ RTA (rapid thermal annealing) [87] to improve their performance. These devices gave a green EL emission with luminance over 600 cd/m$^2$ and an efficiency
approaching 1 lm/W when driven at 1 KHz. Devices were also fabricated using low-pressure chemical vapor deposition [88] and dip-coating [89] techniques for depositing the light emitting layers. Flynn et al. [90] has reported TFEL studies of ZnGa$_2$O$_4$:Mn with an effort to investigate the EL characteristics of the phosphor when post-annealed at lower temperatures. ACPEL devices have also been fabricated by several groups using Mn (Cr) activated ZnGa$_2$O$_4$ as the active layer with luminescent efficiency approaching 15 lm/W [91, 92].

1.10 Zinc Gerenate- Zn$_2$GeO$_4$

Zn$_2$GeO$_4$ is also a ternary oxide phosphor, whose structure is similar to Zn$_2$SiO$_4$, where Si is replaced by Ge. The most prominent advantage of Zn$_2$GeO$_4$ over Zn$_2$SiO$_4$ is its low crystallization temperature. The band gap of Zn$_2$GeO$_4$ is 4.57 eV. However in the literature, reports on Zn$_2$GeO$_4$ phosphor are scarce.

The bulk phosphor prepared by solid state reaction is reported to be an intrinsically defect phosphor [93]. By doping Zn$_2$GeO$_4$ using Mn, the phosphor emits intense green light at 535 nm.

Thin films of Zn$_2$GeO$_4$:Mn$^{2+}$ have been deposited using rf magnetron sputtering [94-97] and PLD [98]. Improved luminescent characteristics have been obtained using post-deposition annealing in this phosphor material. However the thin film phosphor emits green light relatively low annealing temperature (650 – 700°C) via furnace annealing and at 125°C via hydrothermal annealing [99]. ACTFEL devices were also fabricated using sputtered Zn$_2$GeO$_4$:Mn as active layer [95-98]. Minami et al. has reported a highest luminance of 1536 Cd/m$^2$ from Zn$_5$Si$_{0.5}$Ge$_{0.5}$O$_4$ at 60Hz drive frequency from the Thick dielectric electroluminescent (TDEL) devices fabricated on ceramic BaTiO$_3$ substrates [97]. In all these cases the active layer was deposited using rf
magnetron sputtering. The effect of substrates and deposition parameters on luminescence of laser ablated $\text{Zn}_2\text{GeO}_4\cdot\text{Mn}$ was studied by Williams et. al [98]. Lewis et. al has fabricated a green ACTFEL device on glass substrates via rapid thermal annealing (RTA treatment on the deposited phosphor layer. The anneal temperature was 860°C. Baker et al. has fabricated EL device on Si substrates as a light source for integrated optics systems [99]. The active layer was sputtered $\text{Zn}_2\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}_4$.

### 1.11 Yttrium oxide - $\text{Y}_2\text{O}_3$

Since the early 20th century, it has been known that crystals containing a small amount of rare earths emit characteristic luminescence lines, not bands, in the visible spectral region when the crystals are irradiated under an electron beam, ultraviolet light, and X-rays. The luminescence lines are assigned to the radiative transitions in the 4f$^n$ shell of rare-earth ions, which are well shielded electrically with the electrons in the 5d and 6s shells. Because of line luminescence, rather than broad band, scientists paid attention to the crystal field effect, e.g., Stark effect, on rare-earth luminescence. In that time, purification of rare earths was difficult. Rare earths are chemically very close to each other, so that ordinary techniques of analytical chemistry could not separate one from the other. In the late 1960s, YVO$_4$:Eu (laser material) was proposed as a phosphor for the red primary in color TV picture tube screens [100]. They claimed improvement of brightness and color fidelity of the screen, thus opening the door for industrial use of yttrium oxide ($\text{Y}_2\text{O}_3$) and europium oxide ($\text{Eu}_2\text{O}_3$), and subsequently other rare earths. The red primary phosphor shifted from YVO$_4$:Eu to $\text{Y}_2\text{O}_3$:Eu, $\text{Gd}_2\text{O}_3$:Eu, and finally $\text{Y}_2\text{O}_2\text{S}$:Eu. Among the above mentioned
phosphors, being an oxide phosphor, $Y_2O_3$:Eu has created much interest among the researchers around the world.

### 1.1.1 Crystal structure

![Crystal structure diagram](image)

**Figure 1.8** Two different types of crystal structures in $Y_2O_3$ unit cell; $C_2$ (vacancies along face diagonal) and $S_6$ (vacancies along body diagonal)

Yttrium oxide has a cubic C-type or bixbyte ($Mn_2O_3$,) structure in which eight incomplete fluorite formula units exist with 80 atoms (yttrium:32 and oxygen:48) and a lattice constant $a = 10.60 \ \text{Å}$ in the unit cell (figure 1.8). While in an ideal fluorite structure ($CaF_2$) each cation is surrounded by eight anions located at the eight cube corners, the structure of $Y_2O_3$: Eu is modified
from the ideal fluorite structure by removing a quarter of oxygen atoms to maintain the charge neutrality and then rearranging the remaining six oxygen atoms from the cube corners. Therefore, each yttrium atom is surrounded by only six oxygen neighbors forming two different types of distorted octahedral structure (S₆ and C₂ sites, respectively (Fig. 1.8)) in the unit cell. Eight yttrium atoms occupy the S₆ symmetry and 24 atoms are in the C₂ symmetry [101].

1.11.2 Photoluminescence

In Y₂O₃:Eu³⁺, the mechanisms that are governing the absorption and subsequent red emission are 1) direct excitation of the Eu³⁺ ion, 2) excitation via a charge-transfer state between the Eu ion and neighboring O ions or 3) excitation via the Y₂O₃ host lattice [102]. The Y₂O₃: Eu PL emission consists of a large number of lines ranging from 580 – 700 nm and in general these lines can be assigned to ⁵D₀ → ⁷F₃, J=0,1,2,3 transitions of Eu³⁺ ions. Each of these transitions is partially resolved into various mJ transitions. These emission lines correspond to inner f-f transitions and are electric dipole forbidden. From the emission spectrum, one can speak about local crystal environment of Eu³⁺ ion, especially analyzing the relative intensity ratio of ⁵D₀ → ⁷F₁ and ⁵D₀→⁷F₂ emission lines. The intensities of these transitions highly depend on local crystal environment in different ways [104]. The ⁵D₀ → ⁷F₁ transition is electric dipole forbidden and intensity of this line can be attributed to magnetic dipole operator and almost insensitive to local environment. But ⁵D₀→⁷F₂ transition, by mixing with higher allowed transition, is electric dipole allowed and intensity of which being hypersensitive to local environment (i.e., the local electric field and local symmetry) [103].
Eu$^{3+}$ ions are supposed to replace Y$^{3+}$ 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$^{3+}$ ions resulting in corresponding red PL emission. The emission spectrum consists of several lines which gives information about Eu$^{3+}$ site symmetry in the lattice. In Y$_2$O$_3$, 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$_2$ symmetry), or along face diagonal of a cube (S$_6$ symmetry) \[104\]. Only 1/3$^{rd}$ of the Y atoms occupy S$_6$ symmetry while remaining 2/3$^{rd}$ of atoms occupies C$_2$ symmetry \[104\]. The optical transitions in Eu$^{3+}$ states are more likely to occur in the C$_2$ site rather than in S$_6$ site due to its more stable inversion symmetry of the lattice \[104\]. Therefore only certain magnetic dipole transitions are allowed in the S$_6$ sites, while the electric dipole transitions are preferred in C$_2$ sites. More over S$_6$ site are less in number which will reduce the intensity of PL emission of magnetic dipole transitions. In the observed emission spectra, the lines at 538-585 nm ($^5D_1 \rightarrow {}^7F_1$) corresponds to magnetic dipole transitions while that at 590-715 nm ($^5D_0 \rightarrow {}^7F_j$, $j = 0$ to 4) corresponds to electric dipole transitions which include peak emission maximum 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$^{3+}$ ions are incorporated in to the host lattice and most of the ions predominantly replace Yttrium ions with C$_2$ symmetry.

The bulk form of RE doped Y$_2$O$_3$ has been synthesized using several techniques like flame fusion process \[24\], solid state reaction \[105-108\], citrate gel acid method \[109\], ceramic method \[110\], combustion method \[111\],
simultaneous addition method (simadd) [112] and self propagating high temperature synthesis [113]. Stimulated emission from single crystals of Y$_2$O$_3$:Eu have been reported [24]. Enhanced cathodoluminescence has been observed from Y$_2$O$_3$:Eu phosphor on co-doping with La, Li and Zn [107, 108, 110]. A white emission has been achieved from Y$_2$O$_3$ doped with Eu and Sm, when excited with UV-LED showing it as an excellent phosphor for white LEDs [109]. The thin films of doped and undoped Y$_2$O$_3$ has been deposited using spray pyrolysis [114, 115], Sol-gel technique [116-118], electron beam evaporation [119], rf magnetron sputtering [120-123], MOCVD [124] and pulsed laser ablation techniques [125-137]. PLD has been widely used to deposit high quality Y$_2$O$_3$ thin films. ACTFEL device using Y$_2$O$_3$:Eu has been fabricated by Suyama et al. in conventional MISISM structure [138]. However no EL could be obtained from the devices. EL was observed when they used ZnS as accelerating layers. Multilayers of Y$_2$O$_3$:Eu and ZnS was deposited on Glass/ITO substrates. Due to low electron transport in Y$_2$O$_3$, EL could not be observed from the devices fabricated without ZnS layer. So ZnS was used to accelerate the electrons as the ZnS have better electron transport property. But high luminance yellow emitting TDEL devices using Y$_2$O$_3$:Mn and combination of {[Y$_2$O$_3$-GeO$_2$] Mn} was fabricated by Minami et al. [139, 140].

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