Chapter 1

A general introduction
1.1. Introduction

Luminescence or ‘weak glow’ [1] is the radiation emitted by a material excessive in comparison to thermal radiation. It results from the transition of an excited electronic state to a ground state or another state lower in energy, the duration of which is much longer than the period of light vibrations ($10^{-10}$ sec). The competing radiationless transitions results from interactions with the lattice or a transfer of energy to other ions. Luminescence, depending on the mode of excitation, is reflected in expressions such as photo-, electro-, chemi-, thermo-, sono-, or triboluminescence. In practice, most often the excitation is via x-rays, cathode rays, or UV emission of a gas discharge. The position of the band in the luminescence spectrum is independent of the method of excitation and is determined only by the interlevel spacing. Two other terms quite often used to classify luminescent materials are fluorescence ($\tau < 10$ ms) and phosphorescence ($\tau > 0.1$ s). As the mechanism of luminescence is associated with the duration of glow, the decay law of luminescence is exponential in fluorescence, and hyperbolic or still more complicated for phosphorescence.

1.2. The phenomenon of photoluminescence (PL)

1.2.1. Basic concepts

The luminescent emission from the mineral barite on exposure to sunlight was identified as ‘photoluminescence’ (PL) first by Vincenzo Cascariolo. A material photoluminesces when excited by monochromatic light or by UV radiation with
a spectrum broad enough to overlap the ion absorption bands. The phenomenon is pictorially illustrated using either a unidimensional diagram of energy levels (in the form of straight lines) or a bidimensional pattern (energy versus interionic distance) of the same levels in the form of configuration curves [2].

The three elementary processes between an ion’s states are: excitation, emission and radiationless transitions. If the interaction between the ion and the lattice is weak, the wavelength of the emission band matches that of the absorption band. For example, the f electrons in trivalent rare-earth (RE$^{3+}$) ions are shielded from the interactions with the lattice. If the interaction is fairly strong, as in transition metal ions, the emission band shifts towards longer wavelength with respect to the absorption band - a relation known as the empirical Stoke’s law [3]. Generally, a rise in the temperature of the system makes it conducive to radiationless transitions and to falling intensity of emission.

Excitation and emission are separated by a time interval ie. by the lifetime of the excited state ($\sim 10^{-8}$ sec or more). This time interval is sufficient for the system to adapt itself to the given excited electronic state which includes shifting of the surrounding (ligand) ions to a new equilibrium position, rearranging the interionic distance and transition to the lowermost of the vibrational levels ($\sim 10^{-12}$ sec) i.e., to the excited electronic level. If a transition occurs between the levels, say, m (excited electronic state) and n (ground state or state of lower energy), the lifetime $\tau_m$ is expressed as,

$$\tau_m = \frac{1}{(\Sigma A_{mn} + \Sigma C_{mn})}$$  \hspace{1cm} (1.1)
where, $A_{mn}$ and $C_{mn}$ denote the probability for radiative and nonradiative transitions between the levels. The summation is relevant whenever the transition occurs not over a single but over several sub-adjacent levels.

The fraction of emission transitions with respect to the sum total of emission and radiationless transitions gives the quantum yield $\eta$:

$$\eta = \frac{\sum A_{mn}}{\left(\sum A_{mn} + \sum C_{mn}\right)}$$

(1.2)

If there are $N_m$ photons in the excited state initially, the exponential law of luminescence decay states that after a time $t$,

$$N(t) = N_m e^{-t/\tau_m}$$

(1.3)

A direct relation exists between the emission intensity and the probability $A_{mn}$ of emission transition given by,

$$I_{em} = N_m \hbar \nu_{mn} A_{mn}$$

(1.4)

Thus, shorter the lifetime of the excited state i.e. time for photon emission, more intensive shall be the glow. Conversely, the greater the probability $C_{mn}$ of radiationless transition, the lesser the intensity of glow and hence the quantum yield. The greater the oscillator strength for a given transition, higher shall be the intensity of the emission, provided radiationless transitions are absent.

Photoluminescence is divided into two major kinds: intrinsic and extrinsic depending on the nature of electronic transition producing it.
1.2.2. Intrinsic luminescence

There are three kinds: band-to-band luminescence, exciton luminescence and cross luminescence.

1.2.2a. Band-to-band luminescence:

The recombination of an electron in the conduction band with a hole in the valance band generates band-to-band luminescence. This kind of luminescence is observed in pure crystals at relatively high temperatures. Eg: Si, Ge and IIIb-Vb compounds such as GaAs. The light emission from bright light emitting diodes and semiconductor lasers is usually due to band-to-band transition process.

1.2.2b. Exciton luminescence:

An exciton moves in a crystal conveying energy and produces luminescence owing to the recombination of the electron and the hole. There are two kinds of excitons: Wannier exciton and Frenkel exciton.

The Wannier exciton model expresses an exciton as composed of an electron in the conduction band and a hole in the valence band bound together by the Coulomb interaction. The expanse of the wavefunction of the electron and hole is much larger than the lattice constant. This kind of luminescence is observed in inorganic semiconductors such as IIIb-Vb and IIb-VIb compounds. Wannier
excitons are stable only at relatively low temperatures, where the binding energies of excitons are higher than the thermal energy. At higher temperatures, excitons are no longer stable, and band-to-band luminescence appears instead.

The Frenkel exciton model is used in cases where the expanse of the electron and hole wave function is smaller than the lattice constant. Typical examples are organic molecular crystals and inorganic complex salts. In these materials, the excited state of an isolated molecule or a complex ion transfers from molecule to molecule or from complex ion to ion usually owing to dipole-dipole interactions. It is therefore regarded as the exciton state. Luminescence characteristics are similar to those of isolated molecules or complex ions.

1.2.2c. Cross luminescence:

Cross luminescence is produced by the recombination of an electron in the valance band with a hole created in the outer most core band [4]. This is observed in a number of alkali and alkaline earth halides and double halides. This occurs only when the energy difference between the top of valance band and that of the outermost core band is smaller than the band gap energy. Or else, an auger process occurs selectively. The shape of the spectra reflects the grouping of the molecular orbitals in the clusters involving cations with a hole in the core shell and nearest neighbour halide ions. For crystals with more than one type of cation, the spectrum reveals information about the 'active' cation which contains the core hole and also about the other cations. A notable characteristic of cross luminescence is that the decay time is very fast, of the order of
nanoseconds or less, and hence such luminescent systems are used as scintillators.

1.2.3. Extrinsic luminescence

Luminescence caused by intentionally incorporated impurities (or activators) is classified as extrinsic luminescence. Most of the observed types of luminescence that have practical applications belong to this category. Extrinsic luminescence in ionic crystals and semiconductors is classified into two types: unlocalized and localized.

1.2.3a. Unlocalized type:

In the unlocalized type, the electrons and holes of the host lattice, i.e., free electrons in the conduction band and free holes in the valence band, participate in the luminescence process. This includes two kinds of luminescence transitions, namely the transition of a free carrier to a bound carrier and the transition of a bound electron at a donor to a bound hole at an acceptor. These kinds of luminescence lines and bands are usually observed in compound semiconductors such as IIIb-Vb and IIb-VIb compounds.

1.2.3b. Localized type:

Here, the luminescence excitation and emission process are confined in a localized luminescence center. Various kinds of metallic impurities intentionally
incorporated in ionic crystals and semiconductors often create efficient localized luminescence centers. Localized type centers are classified into allowed and forbidden transition type in terms of electric dipole transitions. The electric dipole transition can take place between energy levels only with different parities ie. $\Delta l = \pm 1$, $l$ being the azimuthal quantum number. When atoms and ions are incorporated in crystals, the forbidden character of the dipole transition is altered by the perturbation of the crystal electric field, so that the forbidden transition becomes allowed to some degree.

(i) **Allowed transition type:**

1. $s \leftrightarrow p$ transition - F centre $\leftrightarrow$ (an electron trapped at an anion vacancy), $\text{Tl}^0$
2. $s^2 \leftrightarrow sp$ transition - $\text{Ti}^+$, $\text{Sn}^{2+}$, $\text{Pb}^{2+}$, $\text{Sb}^{3+}$, $\text{Bi}^{3+}$
3. $f \leftrightarrow d$ transition - $\text{Eu}^{2+}$, $\text{Ce}^{3+}$

Oscillator strength for this type of transition is of the order of $10^{-1}$-$10^{-3}$ and the luminescence spectra have a broad bell shaped appearance.

(ii) **Forbidden transition type:**

1. $d \leftrightarrow d$ transition - $\text{Ti}^{3+}$, $\text{Cr}^{3+}$, $\text{Cr}^{2+}$, $\text{Mn}^{4+}$, $\text{Mn}^{2+}$, $\text{Fe}^{3+}$, $\text{Fe}^{2+}$

Iron group ions show luminescence owing to the $3d^{n^*} \leftrightarrow 3d^n (n = 2-8)$ transition in the visible to infrared region. Among them, $\text{Cr}^{3+}$ and $\text{Mn}^{4+}$ ions with $3d^3$ configuration and $\text{Mn}^{2+}$ ion with $3d^5$ configuration are important for phosphor
applications. Spectra of transition metal ions comprise of either broad bands or characteristic lines.

2. f \leftrightarrow f \text{ transition - } \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Tm}^{3+}, \text{Dy}^{3+} \ (\text{and other trivalent rare earth ions})

Most trivalent rare earth (RE) ions give efficient line spectra owing to the $4f^{n} \leftrightarrow 4f^{n}$ transition in the visible to near IR region. Among them, Eu$^{3+}$ ion (red) and Tb$^{3+}$ ion (green) are excellent activators for various practical phosphors. Absorption and emission spectra due to f-f transitions are rather sharp lines. As the 4f energy levels are well shielded by the 5s5p shells, they are weakly influenced by crystal field perturbations. So their emission does not change much with host lattice. Oscillator strengths of this type of transition, made allowed, are of the order of $10^{-4}$-$10^{-8}$.

1.2.4. Energy transfer in luminescence: sensitization

If the phosphor host itself is self-luminescent or if there are two or more activators in a phosphor, an interaction can take place between the luminescent centers which shall be expressed in their luminescence spectra. The absorption spectra of the phosphor, in such cases, shall be a superposition of each of their absorption spectra. As for the emission spectra, the position of emission lines of each of them does not change in the presence of the other, i.e., superposition of the emission spectra occurs but with any of the following changes:
(1) the luminescent intensity of one ion can gain in strength at the expense of the diminishing intensity of the other,

(2) an ion not luminescent at a given concentration in a phosphor system becomes luminescent in the presence of the other ion in a different system,

(3) luminescence of an ion can be observed under conditions of an excitation (in the absorption band of another ion) in which it was not luminescent without the presence of the other ion,

(4) sometimes an ion even exhibits an intensified luminescence with complete quenching of the other.

Such luminescence observed in ions excited as a result of energy transfer from other ions that are excited in the absorption band is termed sensitized luminescence, i.e.,

\[
\begin{align*}
S^* & \rightarrow A^* \\
\uparrow & \quad \downarrow \\
S & \quad A
\end{align*}
\]

Here, S is the sensitizer (energy donor) and A is the activator (energy acceptor); asterisks denote their excited states. It is usually observed in phosphor systems, with Mn\(^{2+}\) and RE\(^{3+}\) ions as activators, which do not possess suitable excitation bands (band-to-band excitation is possible only at very high energies and merely narrow and weak absorption lines are associated with forbidden f-f transitions). This limitation is overcome by incorporating into the system a sensitizing ion with a suitable absorption band. Conversely, Cr\(^{3+}\), RE\(^{2+}\) and other ions
themselves have the ability to present broad intensive absorption bands suitable for inducing luminescence.

![Diagram showing sensitized luminescence](image)

**Figure 1.1.** Sensitized luminescence: (a) Emission-reabsorption, (b) Resonance radiationless and (c) Nonresonance radiationless

In sensitized luminescence, the absorption band of the activator ions must overlap with the emission band of the sensitizer ions. In other words, the energy absorbed in the absorption band of the sensitizer ion is emitted in the emission band of the activator ion. Energy transfer from sensitizer to activator can occur in three different ways, the illustrations of which are shown in figure 1.1.

1.2.4a. **Emission-reabsorption:**

In this case, the light emitted by the sensitizer ion (primary luminescence) is re-absorbed and later emitted (secondary luminescence) by the activator ion. Both the sensitizer and the activator have intense absorption bands and behave as
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independent systems which interact directly. The closer the emission energy of one to the absorption energy of the other, the more probable is the energy transfer to occur. An example is the intensification of Nd$^{3+}$ luminescence in the presence of Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$ and Dy$^{3+}$.

1.2.4b. Resonance radiationless energy transfer

The resonance radiationless energy transfer mechanism is effected between interacting ions behaving like a single system. The sensitizer may not be necessarily emissive and the activator ions may not have sufficiently intensive absorption bands suitable for inducing luminescence. But the broad absorption bands of the sensitizer and the emission transitions of the activator together comprise a system capable of effective luminescence. Since a resonant energy transfer can be obtained between an allowed transition in the sensitizer and forbidden transition in the activator, this kind of mechanism is the prime cause of sensitized luminescence in inorganic luminescent systems.

The process of energy transfer is effected by dipole-dipole or dipole-quadrupole interactions between ions, the probability of the transfer being proportional to $r^{-6}$ or $r^{-8}$ respectively, where $r$ is the mean distance between the interacting ions. Here, the reduced duration and decreased quantum yield of the sensitizer emission is compensated by the longer duration and greater quantum yield of the activator's luminescence. The probability of the energy transfer increases proportionally to the diminution of the mean distance between ions, reduction of the lifetime of sensitizer in an excited state and to a greater overlap of the
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sensitizer's emission and activator's absorption. The decay curve, instead of
being purely exponential, is a sum of exponential curves.

1.2.4c. Nonresonance radiationless energy transfer

The nonresonance radiationless energy transfer mechanism occurs in the event
of a substantial nonconcurrence of distances between the levels of ion
transferring the energy and the levels of the ion receiving the energy. This
involves an exchange interaction between ions and comes into play over very
short distances. Sensitization is therefore accomplished by impurity
incorporation or lattice modifications. The energy is transferred to any pair of
the acceptor levels (which need not be long living and emissive) whose distance
is the closest to the energy transmitted by the sensitizer ion. Regardless of the
fact to which pair of the acceptor levels the energy is transferred they become
deactivated by means of rapid radiationless transitions to the radiation level from
which the final emission occurs.

1.2.5. Concentration quenching (self-quenching)

If the energy transfer occurs from an emitting center to a nonradiative center,
luminescence gets quenched. Such a change in luminescent intensity is
manifested in various ways for different activators. Generally, the intensity of
the glow passes through a maximum and then diminishes with growing
concentration of the activator. This depends on the mechanism of interaction
between these ion activators of the same kind.
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(1) The emission-reabsorption energy transfer between ions of the same kind can lead to self-absorption, for eg., self-absorption of Cr$^{3+}$ ion.

(2) The most common means of concentration quenching is nonradiative resonance multipole energy transfer between ions of the same type, as in many trivalent REs.

(3) An exchange mechanism of concentration quenching becomes apparent in the case of ions that fail to have coincident differences of the emission and radiationless levels of transitions (as for Eu$^{3+}$).

1.3. The phenomenon of electroluminescence (EL)

Electroluminescence is the direct, nonthermal conversion of electrical energy into luminous energy. The first observation on the effect of electric fields on luminescence was reported by Gudden and Pohl in 1920 [5]. Still, the famous paper by George Destriau in 1936 [6] is often cited as the first published report on electroluminescence. Destriau observed light emission from a suspension of ZnS:Cu dispersed in castor oil when subjected to ac fields.

A breakthrough in EL technology was made in 1974 by Inoguchi et al. (Sharp Corporation) [7], who was able to establish thin film EL (TFEL) cells based on ZnS:Mn, which had both higher efficiency and a reasonable lifetime. The key to this approach was the concept put forward by Russ and Kennedy [8] which described a three layer sandwich design. The highlight of the Inoguchi structure was that the insulators completely encapsulate the active layers and serve as buffers, shielding the device from breakdown when local current densities are
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high. The high reliability of the structure and the fair reproducibility of the device characteristics due to improved thin film deposition techniques helped one to investigate the physical aspects of high field EL more precisely from the aspect of fundamental research. This innovation is credited with transforming the research and development of electroluminescence into a viable display technology.

Today, both thin film and powder EL displays are active in the market place. While both ac and dc driven devices have been explored for display applications, the interest in ac driven thin film electroluminescent devices has dominated. Since the thesis is focused on ac thin film EL devices, the structure and physics of ACTFEL devices are discussed briefly.

1.4. ACTFEL devices

There are two classes of EL devices - Injection EL or low field EL (\(\sim 10^4 \text{ V/cm}\)) based light emitting diodes (LED) and high field EL (\(>10^6 \text{ V/cm}\)) based TFEL displays. Both are distinct physically and fundamentally. The TFEL devices differ in principle from standard LEDs and diode lasers. In the former, the generation of light is by the impact excitation of light emitting centers by high energy electrons accelerated by an electric field whereas in the latter, electron-hole recombination near a p-n junction is responsible for luminous emission. To achieve sufficient diffusion length of the minority carriers and radiative recombination in the low field regime, single crystalline materials are needed for
LEDs and diode lasers. Polycrystalline films can be used in high field EL, which is a considerable advantage of thin film EL displays.

| Ac drive       | Ac thin film                  | • High resolution, matrix drive  
|                |                                | • Long lifetime                  
|                |                                | • Multicolor and full color capabilities|
| Ac powder      |                                | • Backlight for liquid crystal displays (LCD)  
|                |                                | • High luminous efficiency        
|                |                                | • Short lifetime.                 |
| Dc drive       | Dc thin film                   | • Reliability problem            |
|                | Dc powder                      | • Low voltage matrix drive        
|                |                                | • Multicolor capability           |

Table 1.1. Comparison between the four types of EL displays

High field EL devices have been categorized into four based on the drive voltage waveform and the phosphor configuration: ac thin film EL (ACTFEL), ac powder EL (ACPEL), dc thin film EL and dc powder EL. Table 1.1 outlines some comparative remarks on the four kinds of EL devices.

DCEL has been widely used for small displays on glass in automotive environments usually as yellow fixed messages and for backlighting purposes. ZnS:Mn based ACTFEL displays used as flat screens of laptop personal computers and word processors and ACPEL devices used as backlights for liquid crystal displays are today commercially available.
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Powder EL displays have virtually unlimited potential, i.e., uniform light emission, thin profile and low power consumption [9]. Flexible powder EL devices can be made on polyethylene terephthalate (PET) coated indium tin oxide (ITO) substrates [10, 11]. Powder EL lights have been used for architectural and decorative lighting and as 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 hrs). With the development of thin film technology in the 1960's, the initial efforts to utilize the phenomenon of electroluminescence on powder EL devices turned to 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 outgassing, and better adhesion to the solid surface [12]. 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.

An ACTFEL display possesses several unique features:

Solid state nature: The solid state construction renders an ACTFEL device extreme ruggedness making them more resistant to shocks and vibrations. They
can, therefore, withstand aggressive environments, such as cold, heat, wind, dust, sunlight, a characteristic desirable for displays used in military equipments and spacecrafts. The luminous emission in a solid state environment also eliminates the risks involved in maintaining a vacuum or plasma environment. Moreover, the solid state nature enables it to be fully integrated onto the substrate of the drive electronics.

**Wide viewing angle:** The emissive EL displays offer a viewing angle greater than 160° which has been an inherent problem with LCDs. 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 (-25°C to 65°C), often limited by the drive electronics, and therefore can serve in many critical military and industrial applications. They don't freeze or get get slow or dim even at low temperatures.

**Long life:** The panel itself has no significant wearout 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. Such high legibility is the strongest selling point of TFEL displays.
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**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 flat panel displays (FPDs) with the image quality of the cathode ray tubes (CRTs).

ACTFEL displays overrule LCD’s, that make almost 90% of the current FPD industry, in their ability to pattern much smaller pixels, performance over a wide temperature range, wide viewing angle and readability with much greater intensity background light. The disadvantages of ACTFEL displays over LCD’s are larger power consumption, much larger driving voltages and the lack of adequate chromaticity of the three primary colors.

1.4.1. ACTFEL device structure

There are three general configurations for thin film EL device structures as shown in figure 1.2 - (a) doubly insulated standard MISIM (metal-insulator-semiconductor-insulator-metal) structure, (b) doubly insulated inverted MISIM structure and (c) singly insulated structure.

The most frequently used ACTFEL structure is the ‘standard’ double insulating layered structure on a transparent glass substrate. Here, the phosphor material is sandwiched in between two dielectric layers. The bottom electrode is transparent and the top electrode is opaque. In the ‘inverted’ double insulating layer structure, the electrodes are simply inverted and so the light emission now takes place in the opposite direction unlike that in the standard case. The advantage is
that opaque substrates like silicon which could withstand higher temperatures can be used as in active matrix electroluminescent (AMEL) [13] displays as well as thick film dielectric hybrid electroluminescent (TDEL) displays [14].

![Diagram](image)

**Figure 1.2.** (a) Standard MISIM (b) Inverted MISIM and (c) Single insulating ACTFEL structures

AMEL displays typically use silicon substrates that allow the drive electronics and the EL device to be manufactured on the same substrate. High performance displays with a resolution of 2000 lines per inch (LPI) have been manufactured with this technology. AMEL technology is employed in helmet mounted or heads-up display applications, which include commercial virtual reality games and military flight simulators. The TDEL technology uses an opaque alumina substrate on which they screen print an opaque high dielectric constant ferroelectric thick film as one of the insulating layers. There are several advantages of the thick film hybrid EL approach, namely (1) the alumina substrate is stable at high temperatures above the softening point of a glass
substrate, (2) higher dielectric constant insulators can be used, and (3) thick film processing is inherently cheaper than thin film processing. Most ACTFEL phosphors become brighter and more efficient as the annealing temperature increases. In multicolor displays, color filters are often employed to provide saturated or pure red, blue, and green color components. These filters, typically dyed organic materials, are usually positioned in between the phosphor and the emitting side of the display. Because the filters cannot withstand the temperatures needed to process the other layers of an ACTFEL device, they must be deposited last on the top of the device and this necessitates the use of the inverted structure. One disadvantage of this approach is that the pixel resolution is limited due to the surface roughness of the substrate.

Apart from these, single insulating layered structures are also practiced. Here, the EL oxide phosphor is directly deposited either onto a thick BaTiO$_3$ insulating layer or onto a BaTiO$_3$ ceramic sheet. The former structure avoids chemical reaction of the phosphor layer with the BaTiO$_3$ substrate during post-annealing. In the latter structure, the ceramic substrate serves a double function of the device substrate and of an insulating layer between the substrate and the EL phosphor. Moreover, the BaTiO$_3$ ceramic sheet substrate can be utilized primarily for high temperature annealing above 1000$^\circ$C.

The replacement of a Si substrate for the BaTiO$_3$ ceramic sheet is beneficial to avoid undesirable chemical interactions with the EL phosphor. Furthermore, Si is suitable for high resolution electrodes for active/passive matrix addressing, whereas BaTiO$_3$ substrate is impractical to do so.
1.4.2. The ideal model

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 threshold and a pair of back-to-back diodes above threshold [15]. The equivalent circuit model shown in figure 1.3 very well demonstrates the essential phenomenological physics of a thin film EL device.

![Equivalent circuit of an ideal ACTFEL device and Ideal I-V characteristics of the nonlinear resistor of the phosphor layer](image)

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

Below threshold, 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

\[
C_I = \frac{C_{I1}C_{I2}}{C_{I1} + C_{I2}} \tag{1.5}
\]
where $C_{l1}$ and $C_{l2}$ are capacitances per unit area of the first and second insulating layers, respectively. The thin film phosphor behaves as a capacitor below the threshold voltage $V_{th}$ with the capacitance per unit area $C_{EL}$. 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 nonlinear resistor with the ideal I-V characteristic as shown in figure 1.3. In an ideal case, this nonlinear resistor can be simulated by back-to-back Zener diodes. The luminance of the device is proportional to the power consumed in this resistive branch with the proportionality constant being the experimentally determined luminous efficiency $\eta$ in units of lumens per watt (lm/W).

Factors like transferred charge density, power dissipation and luminance that determine the device performance can be expressed in terms of device parameters such as layer thickness, dielectric constant, dielectric breakdown strength, threshold field and luminous efficiency based on the ideal model considerations [16]. The model even explains most of the observed thin film EL device characteristics except the time dependence of charge transport [17, 18].

1.4.3. ACTFEL device physics

The basic function of each layer of a TFEL device is the same irrespective of whether the structure used is the standard or the inverted MISIM. The solid state processes are summarized in figure 1.4. The vertical axis represents energy. The band is tilted from the cathode side of the phosphor layer to the anode side as a
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voltage drop is applied across the phosphor layer. The physical processes involved in high field EL are [9]:

Figure 1.4. Mechanisms that occur in an ACTFEL device

1. **Electron injection** from insulator/phosphor (IS) interface states into the conduction band of the active layer
2. **High field charge transport** i.e., the subsequent acceleration of the carriers in the phosphor layer at high electric fields to optical energies
3. **Impact excitation** of luminescent centers by energetic electrons
4. **Electron re-capture** at the opposite IS interface leading to polarization effects
5. **Radiative de-excitation** of the luminescent centers
6. **Radiative out-coupling** of the generated photons
1.4.3a. Electron injection

In capacitive coupled ACTFEL devices, the carriers are injected from the IS interfaces rather than from the external electric circuit when the phosphor field exceeds a threshold value. There are several reasons to state that the interface is the source of carriers. The discontinuity in the periodic lattice structure at the IS interface results in dangling chemical bonds that creates electronic states within the forbidden gap (Tamm states). The depth and concentration of the available interface states changes significantly with the choice of the dielectric. Also, the threshold field for charge transfer gets modified with a change in the nature of the insulator or its deposition methods [19]. Moreover, it has been observed that devices with different top and bottom insulators generate asymmetric device currents and threshold fields as a function of the polarity of the applied voltage [20]. Deeper the interface state, least probable is the electron injection process until extremely high fields are reached. Conversely, if they are too shallow, electrons will inject at low fields and will not be accelerated to high enough energies to promote luminescence. The optimum interface trap depth is a rather delicate balance between the two competing processes. Electron state depths 0.6 to 1.3 eV below the conduction band minimum have resulted in good device performance [19, 21].

The electron injection into the conduction band of the phosphor layer can occur via tunnel injection or field assisted thermal ionization (Schottky emission). But the fact that the electrical properties of an ACTFEL device are only a weak function of temperature, compared to what one would expect for Schottky
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emissions, rules out a strict thermionic emission process [19, 22]. So the predominant carrier injection mechanism is assumed to be Fowler-Nordheim tunneling (temperature insensitive) [21]. Reports [23] also say that pure tunneling is the dominant electron ejection process from deep traps at the interface during the leading edge of the applied voltage pulse while phonon assisted tunneling (PAT) of electrons from shallower interface states is the relevant mechanism at the trailing edge and between the pulses. Pure tunneling, however, is the more dominant process above fields $\geq 1 \text{ MV/cm}$ and PAT prevails for relatively small residual fields ($\sim 0.3 - 0.4 \text{ MV/cm}$) [23].

As tunneling was the dominant mechanism of electron injection, one can expect an improved device performance on increasing the density of occupied states by modifying the phosphor/insulator interface. Several groups have reported an increase in the charge injected into the phosphor layer in yellow ZnS:Mn [24-26] and blue Ca$_x$Sr$_{1-x}$Ga$_2$S$_4$:Ce [27] phosphors by introducing a thin interfacial layer between the phosphor and the insulating layer. Rack et al. even reports that the addition of a ZnS layer (30 nm) beneath the Ca$_x$Sr$_{1-x}$Ga$_2$S$_4$:Ce phosphor layer even facilitated the crystallization of the amorphous as-deposited phosphor material during the post-deposition anneal, that in turn improved the device performance.

1.4.3b. High field charge transport

The electron energy distribution inside the active phosphor layer is a complicated function of high field scattering mechanisms such as intervalley
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scattering, polar optical phonon scattering, acoustic phonon scattering, ionized impurity scattering, band-to-band impact ionization and impact excitation [28]. These scattering mechanisms governing the electronic transport in high field EL materials solely depend on the energy band properties of the host phosphor. Most studies show that electron-electron interaction does not play a significant role in high field charge transport. The electrons are transported across the active layer under the combined force of the electric field and the scattering potential mainly by electron-phonon (e-ph) interactions. Polar longitudinal optical scattering, referred to as Frohlich scattering [29], with phonons of low momentum causes only small changes in electron momentum so as to scatter them along the direction of the electric field. Scattering with neutral impurities is negligible at 300 K as the corresponding scattering rates are very low compared to e-ph scattering rates [28]. Ionized impurity scattering plays an important role for mobility in the low field region (<0.1 MV/cm) but scattering rate decreases with electron energy and therefore doesn’t affect the transport behavior at fields ≥ 1 MV/cm.

Several models have been proposed to explain high field electron transport in sulphide based ACTFEL devices. Brennan’s Monte Carlo simulations [30] predict that only 1% of the carriers gain energy > 2 eV at an electric field of 1 MV/cm and 50% at 2 MV/cm. The modified Monte Carlo simulations of Bhattacharya et al. [28] predicts 26% of the carriers to gain energy > 2 eV at 1 MV/cm and 65% at 2 MV/cm. The lucky drift theory modified by Bringuier [31, 32] suggests that 27% of the carriers gain energy above 2 eV at 1 MV/cm and
72% at 2 MV/cm. Only the model by Mach and Muller [33], based on ballistic acceleration, predicts that all electrons turn hot for fields around 1 MV/cm.

1.4.3c. Impact excitation/ionization

Under the influence of the high applied electric fields (~10^6 MV/cm), the accelerated charge carriers turn ‘hot’ (referred so as their energy is much higher than the mean energy at thermal equilibrium). Those that gain sufficient energy promotes an electron in the ground state of the luminescent center either into a higher atomic state of the luminescent center or into the conduction band of the host material, referred to as impact excitation [31] or impact ionization [34] respectively. When the electron is impact excited, it relaxes back into its ground state either radiatively or nonradiatively. For a given dopant concentration and free charge carrier density, the impact excitation probability depends on the radiative cross section of the luminescent center and the energy distribution of the charge carriers. When an electron is impact ionized, the excited electron is immediately accelerated toward the anode by the electric field. Subsequent light emission from the ionized luminescent center requires that an electron be recaptured from the conduction band. Such a two step EL process alters the relaxation kinetics as compared to impact excited centers [32].

1.4.3d. Electron capture

In contrast to dc driven EL devices, the carriers do not leave the semiconductor because of the potential barrier at the IS interface. At the end of the voltage
pulse, the carriers get thermalized (releases energy as heat to the lattice) and are trapped in deep levels at the anodic phosphor-dielectric layer interface. The resultant “polarization charge” has two profound effects on device operation.

First, these charges counteract the applied voltage, acting as a negative feedback mechanism making it increasingly more difficult to inject more charge from the cathode. Second, a non-zero polarization field exists even when the external applied voltage is zero. This field, however, has two consequences. On the one hand, it is responsible for the “leakage charge” that flows across the device when the applied voltage is zero in the charge-voltage characteristics of the device. On the other hand, this polarization field adds to the external field if the subsequent pulse applied across the device has an opposite polarity. Thus, the phosphor threshold field is now reached at a lower external applied voltage than the threshold voltage, a voltage termed the ‘turn on voltage’. The lowering of the turn on voltage and the transferred charge amplification is repeated in the following half cycles of an ac supply. This process continues until a steady state operating condition is established.

1.4.3e. Radiative de-excitation

When an impurity center is in an excited state, the energy will eventually be dissipated. The relaxation process can occur by either 1) emission of a photon, 2) nonradiative relaxation which can be in the form of emission of one or more phonons to the lattice etc, or 3) energy transfer to another center. For display
applications, it is desirable to maximize the first process and to minimize the second. The third case can be useful or harmful in different situations.

1.4.3f. Radiative outcoupling

Only a fraction of the generated photons are out-coupled from the system through the transparent surface along a direction normal to the emitting surface. If one assumes that charge injection and storage occur only at the IS interfaces [35], the total efficiency $\eta_{\text{tot}}$ is the product of three partial efficiencies, i.e.,

$$\eta_{\text{tot}} = \eta_{\text{exc}} \eta_{\text{rad}} \eta_{\text{out}}$$ (1.6)

Of all the electrons that traverse the active layer, not all excites the luminescent centers. Hence, the excitation efficiency $\eta_{\text{exc}}$ gives the ratio of the number of luminescent centers excited to the total charge transferred across the active layer. Of all the impact excitations that occur within the phosphor, not all decays radiatively. The radiative efficiency $\eta_{\text{rad}}$ expresses the ratio of the number of centers decaying radiatively to the total number of luminescent centers excited. Once the photons are generated, all of them do not escape the device in the direction of the viewer. Some undergo total internal reflection and some photons may be lost by absorption and some by reflection. The optical outcoupling efficiency $\eta_{\text{out}}$ is therefore a measure of the number of photons outcoupled to the total number of photons generated within the system.

$\eta_{\text{exc}}$ and $\eta_{\text{rad}}$ are related to the physical processes in the semiconductor layer. $\eta_{\text{out}}$ can be improved by increasing the surface roughness and thereby reducing
internal reflection. However, too rough a surface can reduce contrast because of increased diffuse scattering.

1.4.4. Space charge effects

One of the major deviations from the ideal operation of ACTFEL devices is the formation of space charge within the phosphor layer. Electric field in a ACTFEL device shall be uniform if (1) only IS interface states are involved in free charge carrier supply and trapping and (2) field distortion provoked by the charge flow is low. But there are situations where ionized centers remain in the semiconductor when bulk contributes to charge via thermal or field induced effects, generating a fixed space charge large enough to create a significant field distortion. The removed electron is swept from the ionized trap towards the anode while the trap itself is now positively charged and therefore acts to bend the energy bands locally downwards. The ionized center is usually an intentionally added impurity which acts as a donor due to valence mismatch, a luminescent impurity whose excited state lies close in energy to the conduction band, a vacancy, or another point defect. A second common source of space charge is band-to-band impact ionization of the lattice whereby an additional electron is promoted to the conduction band as a delocalized charge carrier. The hole, left in the valence band, drifts towards the cathode a short distance before it is trapped, resulting in a localized positive charge which, as above, pulls the energy bands downward. The space charge induced curvature of the phosphor layer energy bands is depicted in figure 1.5 for a device under bias. The dotted lines show the spatial dependence of the phosphor layer energy band locations in
the absence of space charge. The linearity of the bands indicates that a uniform electric field exists across the phosphor in the absence of space charge.

Figure 1.5. Space charge induced band bending of phosphor layer in ACTFEL device

A positive space charge enhances the field at the cathodic end than at the anodic side resulting in a nonuniform electric field across the ACTFEL device. As the tunnel emission rate of electrons is a strong function of electric field, it occurs at a lower external voltage (i.e. the ACTFEL device has a smaller turn on voltage) due to the enhanced electric field at the cathodic IS interface. And the reduced electric field at the anodic IS interface results in lesser density of energetic electrons in this region, which reduces the likelihood of impact excitation in this region but may preclude hot electron induced damage to the anodic phosphor-
dielectric interface. Marello et al. [36] has found that the excitation efficiency is lower in the anodic field region in the presence of space charge. Additional higher order effects may also result from the nonuniform electric field. For instance, efficient carrier trapping occurs at the low field anodic region, which may not occur appreciably in the high field cathode region. Moreover, the charge-voltage and luminance-voltage curves of an ACTFEL device exhibit a hysteretic behavior on account of the presence of space charge within the device.

Space charge in ACTFEL devices can be either 'static' or 'dynamic' in nature. 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 wave form, 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 with in one period of the drive waveform.

All well known ACTFEL phosphor systems have been found to exhibit space charge effects. On the one hand, the presence of space charge reduces the voltage necessary for device operation. This should improve reliability and efficiency while reducing driver circuit complexity. On the other hand, the energy expended creating and maintaining the space charge may reduce efficiency, especially when the space charge is dynamic. Once the effects of space charge in a particular system are understood, it may be possible to engineer the space charge in an advantageous way.
1.4.5. Material requirements for ACTFEL devices

TFEL displays are complex optoelectronic devices with challenging material requirements. The multilayered ACTFEL device structure includes two electrodes (of which one is transparent), two insulators, and a semiconducting phosphor layer. Each layer has unique electronic and optical properties that must be satisfied for device operation.

1.4.5a. Substrate

Choice of the substrate checks the EL characteristics and device reliability. Smoothness of the substrate surface influences adhesion and optical properties of the ACTFEL stack. The properties of the substrate often put restrictions on subsequent fabrication steps, such as high temperature annealing and chemical cleaning. The substrate should not interact chemically with other layers of the device and should withstand exposure to processing chemicals and conditions.

Glass substrates, usually employed in EL device fabrication, must satisfy the following physical properties:

(1) high transmission coefficient in the visible region,
(2) thermal expansion coefficient that matches that of the deposited films,
(3) high softening temperature,
(4) low or no alkali metal content, and
(5) high electrical resistivity.
Glass substrates are used because of their transparency, cost and thermal expansion coefficient match to common materials. The commonly used Corning 7059 and NEG substrates are devoid of alkali content, which if diffused into the semiconducting phosphor layer, would result in device degradation with time. But the low softening temperature of the glass substrate restricts high temperature post-deposition treatments that lead to low luminance output. High temperature glass ceramics are also available that typically cost 10 times that of the standard 7059 glass. Si wafers and thick BaTiO$_3$ ceramic sheets are also used as substrates for fabricating EL devices with inverted MISIM structure.

1.4.5b. Electrodes

Two kinds of electrical contacts are needed in ACTFEL devices: opaque and transparent. Atleast one contact needs to be transparent to outcouple the light generated from the device. The materials chosen as electrodes should adhere well to its neighboring layers to prevent delamination. The resistance of the contacts should be minimized to prevent resistive heating of the device and unnecessary power consumption.

(i) Transparent contacts

Transparent conducting electrodes (TCOs) with high conductivity and high transmittance in the visible region are generally used as the transparent electrode of an ACTFEL device. The common example is indium tin oxide (ITO: In$_2$O$_3$ with 10 wt% of SnO$_2$) with a typical sheet resistance of 5-10 ohms/square. Since ITO can be easily etched by normal lithographic techniques, it is suitable for fine
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patterning (~ 8 lines/mm) necessary for high information content FPDs. Other TCO’s used are CdSnO₃, ZnO:Al or amorphous indium gallium zinc oxide.

(ii) Opaque contacts

The requirements of the rear metal electrode for EL applications are:

1. good adhesion to the insulating layer,
2. no metal ion migration at high electric field,
3. no propagating breakdown, and
4. low resistivity.

For the standard structure, the requisites of the opaque electrode are not stringent as it is the last layer deposited. Some of the opaque/metal electrode materials used are Al, Mo, Ta and W. Of these, Al is most frequently used as it can be deposited easily by thermal evaporation. Moreover, Al is inexpensive, highly conductive and reasonably immobile at high fields. However, its high optical reflectivity is undesirable. The engineering tradeoff is that ambient light is also reflected back towards the viewer, apart from the device emission, which can cause contrast problems. The low melting temperature (660°C) of Al is advantageous because Al gets easily vaporized if a short develops within the device; thereby open circuiting the device over a small portion instead of resulting in catastrophic device failure. But this feature of Al restricts its use as the opaque contact in inverted structure ACTFEL devices. Mo and W, preferred in the inverted TFEL structure, must satisfy the additional requirements like:
(1) high melting point,
(2) thermal expansion coefficient that matches that of the substrate,
(3) small reflection coefficient in the visible region to obtain good contrast.

1.4.5c. Insulating layer

The chief objective of an ACTFEL insulating layer is to protect the phosphor layer from catastrophic breakdown under high electric fields. They ensure high stability to the device protecting the phosphor layer against impurities and moisture from outside. The insulating layers must be able to withstand high temperature treatments during fabrication. Also, they must prevent metal ion diffusion into the phosphor layer and provide interface states at the boundary of the phosphor and the insulating layer. The insulator requirements for reliable and efficient ACTFEL devices are:

(1) high dielectric constant,
(2) high dielectric breakdown electric field,
(3) small number of pinholes and defects,
(4) good adhesion, and
(5) small loss tangent.

There are two groups of dielectric materials used in TFEL devices: (a) amorphous oxides and nitrides, such as Al$_2$O$_3$, SiO$_2$, Y$_2$O$_3$, TiO$_2$, Si$_3$N$_4$, Ta$_2$O$_5$, BaTa$_2$O$_6$; (b) ferroelectric materials, such as BaTiO$_3$, PbTiO$_3$. But dielectric materials with high dielectric constant have low breakdown electric field and
vice versa. So a product of the two quantities, referred to as the figure of merit of a dielectric material, is introduced. Moreover, insulating layer materials with a self-healing breakdown mode is generally preferred to those with a propagating breakdown mode.

1.4.5d. Phosphor layer

The active component of the device, that is, the light emitting layer (termed phosphor) consists of two constituents: (1) the host material which dominates the electrical properties of the phosphor layer, and (2) the luminescent center or the activator which dominates the optical properties of the phosphor layer. The host material provides a lattice for the substitutional incorporation of the activator atoms. The activator concentration is of the order of one percent of the host material, which are several orders of magnitude larger than that typically used for semiconductor doping. The essential requisites of an EL phosphor host material are:

(1) A large enough band gap to emit visible light without significant absorption,
(2) Capability to sustain a high electric field (>10^6 V/cm) without breakdown,
(3) Insulating characteristics below the threshold voltage, and
(4) Must be able to withstand the requisite post annealing treatments.

Luminescent impurity requirements are:

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

The crystalline quality and stoichiometry of the phosphor host are critical for efficient incorporation of the activator atoms into the lattice, which in turn determines the efficiency of light emission. The host lattice can influence the color spectrum because different phosphor hosts present different local crystal fields in terms of both field strength and field symmetry. Depending upon the nature of the luminescent transition, the crystal field or a small perturbation may be very important in determining the spectrum of the phosphor.

A good EL phosphor host has the additional and often harder to meet requirement of being able to provide a medium for the efficient transport of high energy (> 2 eV) electrons. This limits the class of possible materials to large band gap (E_g > 2.5 eV) semiconductors and insulators. The classical EL phosphor consists of a ZnS host lattice doped with Mn atoms for the light emission centers.

The nature of the luminescent impurity also determines the spectral emission from a phosphor. For effective incorporation, it is essential that the ionic radii and valency of the activator ion match well with that of the host lattice cation that it replaces. Larger the ionic size of the activator ion, more difficult is the ionic diffusion into the host lattice inhibiting polycrystalline grain growth. Smaller the size, they serve as potential interstitial impurities, subsequently affecting device stability. Moreover, the defects act as nonradiative centers
thereby reducing the device luminance and efficiency. In case of valence mismatch, charge compensation can be achieved intrinsically via vacancy creation (Schottky defects). Charge neutrality by extrinsic compensation can also be achieved by co-doping with monovalent ions such as Na, K or Li occupying divalent cation sites. Such extrinsic charge compensating impurities are referred to as co-activators.

A co-activator functions as a flux agent, compensator or luminescence co-activator, and helps in modifying the luminescent properties of the phosphor. The most effective flux agents are non-isovalent with the constituent atoms of the phosphor host and generate vacancies, thereby improving the atomic diffusion and the host crystallinity. Compensating co-activators are added to accomplish charge compensation in the phosphor host. When activator ions complexes with such defects, a color shift in the luminescence spectra is observed. Blue emitting Ce\(^{3+}\) and Cu\(^{+}\) are efficient luminescent co-activators of red Eu\(^{2+}\) activator that strongly absorbs blue light. The presence of ‘killer centers’ in the phosphor host can also degrade its overall performance [37].

The commercially available sulfide based phosphors often degrade under high energy electron bombardment due to dissociation of the cation-sulphur bonds. This process generates corrosive sulphur bearing gas species that contaminate emission tips and shortens the device lifetime. Due to their hygroscopic characteristics and short term reliability, better substitutes to sulphide phosphors are widely under research. The thermodynamic stability of oxides over sulphides has triggered extensive studies in oxide phosphor materials.
1.5. Oxide phosphors

Oxide thin film phosphors have received considerable attention for use in FPDs owing to their excellent luminescent characteristics, stability in high vacuum, and absence of corrosive gas emission under electron bombardment when compared to sulphide based phosphors. Some long standing problems of sulfide phosphor based TFEL devices such as the lack of primary color emissions and their chemical stability, especially in regard to moisture, have been remedied with the advent of oxide phosphor TFEL devices. They are insensitive to storage and handling in air. Their synthesis is generally easier and safer as no reactive gases are needed during their synthesis whereas reactive gases that other families of materials require for synthesis, sintering and annealing are invariably dangerous and toxic.

But there are several factors that prevent oxides from becoming the dominant class of ACTFEL phosphor. Oxide phosphors, with their large band gaps (compared to sulphides), are generally considered to be incapable of transporting significant current densities of hot electrons, and as such are not traditionally considered as good candidates for efficient EL phosphor hosts. Over the last few decades, a number of efficient oxide EL phosphors have been discovered capable of accelerating electrons to energies ‘hot’ enough to impact excite the luminescent centers.

Another issue regarding oxide phosphors is that their luminance-voltage curves are much less steep than those of sulphides. This inefficient carrier injection is
attributed to their larger effective mass and deeper interface state trap depth that, in turn, leads to non-abrupt device thresholds and larger driving voltages of oxide based ACTFEL devices.

Another serious drawback of oxide phosphors is that they require high temperature processing during and/or post-deposition to achieve a high degree of polycrystallinity, their crystallization temperature lying above 1000°C. This refractory nature limits their deposition by thermal evaporation. Moreover, instead of glass substrates, an inverted structure with a high temperature tolerant substrate and a refractory insulator is therefore preferred for the fabrication of oxide phosphor based ACTFEL devices. In comparison, the deposition of sulphides is less complicated owing to their lower melting point. So they can be easily grown by simple evaporation without the addition of a gaseous species to provide the lost anionic atoms, as sulphur is significantly more condensable than oxygen.

There are several binary and ternary oxides that serve as attractive ACTFEL phosphor candidates. Y$_2$O$_3$ [38, 39] and Ga$_2$O$_3$ [40, 41] are two binary oxides widely investigated as phosphor hosts. A series of undoped and rare earth doped ZnO electroluminors have also been studied [42, 43]. Ternary oxides used in phosphor applications include borates, phosphates, vanadates, tungstates, molybdates, aluminates, silicates, sulphates, germanates, gallates, niobates, titanates and tantalates [44-51]. Among these, silicates and gallates are widely studied, the phosphates and germanates to follow. The alkaline earth phosphates, though investigated, are probably not the best choice for ACTFEL applications.
because both the binary alkaline earth oxides and $P_2O_5$ are moisture sensitive and so shall their compounds be. So they can serve as excellent fluorescent lamp and CRT phosphors due to the presence of an evacuated space for these applications.

Among silicates, $Zn_2SiO_4:Mn^{2+}$ [52, 53] and $Y_2SiO_5:Ce^{3+}$ [54] are widely investigated as low voltage green and blue phosphor respectively. In 1990, Minami et al. fabricated a bright electroluminescent device with an efficiency of 0.15 lm/W by sandwiching a thin film of $Zn_2SiO_4:Mn^{2+}$ between a $BaTiO_3$ sheet and a transparent conducting electrode $ZnO:Al$ [55]. Since then, progressive research efforts were triggered in the field of high brightness, high stability oxide phosphor electroluminescence. Ouyang et al. [56] reported on the fabrication of a multilayered rf sputtered TFEL device using Mn activated $Zn_2SiO_4$ and Ce activated $Y_2SiO_5$.

The substitution of Si by Ge was found to lower the processing temperature. Stuyven et al. [57] reports on the fabrication of ACTFEL devices using the green emitting $Zn_2Si_{0.5}Ge_{0.5}O_4:Mn^{2+}$ phosphor on glass substrates (0.44 lm/W @ 60 Hz) and $BaTiO_3$ ceramic sheets. $Zn_2GeO_4:Mn^{2+}$ have been extensively studied as an efficient green germanate phosphor. An efficiency of 0.45 lm/W has been reported [58] for $Zn_2GeO_4:Mn^{2+}$ active ACTFEL devices fabricated on NEG/ITO/ATO substrates.

Recently, red $Ga_2O_3:Eu^{3+}$ ACTFEL devices have been realized on transparent ITO/ATO glass substrates using pulsed laser deposition [59]. Even higher
efficiencies of up to 10 lm/W have been reported in yellow emitting Y2O3:Mn2+ and (Y2O3)1-x(GeO2)x:Mn2+ [60, 61]. With continued research, commercial oxide phosphor ACTFEL devices may become a reality in the not so distant future.

1.6. White phosphors

White light emitting EL displays have aroused great interest among researchers for producing full color flat panel displays using filters as well as ergonomically suitable white screens, e.g., for word processing displays. It is believed that the latter application would ease the strain on eyes, for instance for a person looking back and forth at black-on-white text and the screen [62].

The color TFEL technology has the potential to produce high performance color FPDs without the complexity of the TFT (thin film transistor) color LCD approach. The development of efficient primary EL phosphors has been the basic challenge for the realization of a practical full color TFEL display technology.

Two parallel avenues are explored for color EL: 1) the development of an efficient white (or broad band phosphor) that can be filtered to produce an RGB display or 2) the development of efficient red, green and blue primary color EL phosphors. The former approach has the advantage of maintaining the simple device fabrication sequence of a monochrome TFEL display (i.e., no patterning of the thin film phosphor or insulator layers) and achieving RGB colors by laminating a patterned color filter to the EL device at the end of the process.
Also, relative to patterning three different phosphors for an RGB or white display, the filtered approach is much simpler to process.

White EL phosphors based on rare earth doped alkaline earth sulfides for filtered color TFEL devices were first reported by the group at Totorri University in 1987 [63]. Since then, white TFEL displays with singly and doubly activated alkaline earth sulfide phosphor layers have been widely investigated [64-66]. White light emitting EL devices have been fabricated by stacking several combinations of the active layers: SrS:Ce/SrS:Eu, SrS:Ce/CaS:Eu [67] SrS:Ce/ZnS:Mn [68]. The highest white luminance of 470 nits @ 60 Hz drive frequency has been reported by Planar International using dual layers of SrS:Ce/ZnS:Mn phosphor deposited by atomic layer epitaxy (ALE).

White light emission has also been realized in certain oxide phosphor systems like CaIn$_2$O$_4$, Sr$_2$SiO$_4$ and SrIn$_2$O$_4$. Partial energy transfer from Ce$^{3+}$ to Eu$^{2+}$ is responsible for white light generation in Sr$_2$SiO$_4$:Eu$^{2+}$, Ce$^{3+}$ [69]. Eu$^{2+}$ has been identified as an efficient sensitizer that transfers energy to Mn$^{2+}$ to result in white light emission under near UV excitation in several phosphor host lattices [70-72]. Singly doped CaIn$_2$O$_4$:Eu$^{3+}$ [73] emits white by an appropriate selection of the dopant concentration. The combination of multicolor emissions from a single luminescence center leads to white light generation in SrIn$_2$O$_4$:Dy$^{3+}$ [74].

The present work suggests a novel white oxide phosphor system - ZnGa$_2$O$_4$:Dy$^{3+}$ - for use in EL devices.
1.7. The ZnGa$_2$O$_4$ phosphor system - a review

In 1991, Itoh et al. [75] was the first to report on a new spinel phosphor system - the ZnGa$_2$O$_4$. It is a ternary oxide compound of ZnO and Ga$_2$O$_3$ comprising of only the fourth row cations. The n-type semiconducting [76] ZnGa$_2$O$_4$ is unique, being a phosphor with cubic symmetry and having an optical band gap of 4.4 eV rendering the material transparency into the UV region of the electromagnetic spectrum.

Zinc gallium oxide crystallizes in the normal spinel structure that has been interpreted as a combination of rock salt and zinc blende structures (figure 1.6). The spinel unit cell belongs to the cubic space group Fd$ar{3}$m (Oh) [77] with eight formula units per cell and contains two kinds of cation sites. In this normal spinel, Zn$^{2+}$ ions occupy tetrahedral sites and Ga$^{3+}$ ions occupy octahedral sites.
with lattice constant $a = 8.37 \text{ Å}$. The oxygen ions are in face centered cubic closed packing. A subcell of this structure has four atoms, four octahedral interstices and eight tetrahedral interstices. This makes a total of twelve interstices to be filled by three cations, one divalent ($\text{Zn}^{2+}$) and two trivalent ($\text{Ga}^{3+}$). In each elementary cell, one tetrahedral and two octahedral sites are filled. 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 spinel structure, hence, turns out to be a close packed cubic arrangement of anions with one-half of the octahedral holes and one-eighth of the tetrahedral holes filled with cations. The material exhibits excellent stability and cubic symmetry in spite of the fact that almost three fourth of the structure is vacant. This is because spinel structures have the ability to accept structural vacancies, thus forming a defect solid solution while remaining as single phase [78].

It is known that oxides with $\text{M}^{2+}\text{M}_2^{3+}\text{O}_4$ spinel structure, in which at least one type of the cation had $d^{10}s^0$ electronic configuration, are promising transparent electroconductive materials. ZnGa$_2$O$_4$ possess interesting UV transparent electroconductive characteristics and therefore can be used for low voltage applications like FEDs. The conductivity of the material at low energy electron excitation can be improved by modifying the phosphor surface, controlling the activator concentration in the phosphor, and adding conductive material to the host material. Moderate conductivity of 30 S/cm has been reported [76] on annealing bulk ZnGa$_2$O$_4$ in a reducing atmosphere at high temperatures. Doping with In [79, 80], W [80], Li [81], Sn [82] and Zn [81] has been reported to generate free carriers in the material by increasing the oxygen vacancy creation.
thereby improving its electrical conductivity. Cu [81] doping was found to increase the scattering and trapping probabilities of electrons, subsequently decreasing the conductivity and luminance of the phosphor.

ZnGa$_2$O$_4$ exhibits an intrinsic blue luminescence under excitation by both ultraviolet light and low voltage electrons via a self-activated optical center associated with the octahedral Ga-O group [83]. The emission properties are relatively sensitive to preparation conditions and Ga/Zn ratio in ZnGa$_2$O$_4$ phosphor [84]. It is reported that the CL spectra of ZnGa$_2$O$_4$ has a peak at 457 [85] or 470 nm [86], while the PL peak is located at about 432 [83], 450 [87] or 470-490 nm [88]. The blue emission can be enhanced by In$_2$O$_3$ doping [79], replacing the cations in the lattice by Li$^+$, Na$^+$ and Ag$^+$ [89, 90] or the anion in the lattice by S, Se and Te [91]. Moon et al. [92] demonstrated that the mixture molar ratio of its constituents, ZnO and Ga$_2$O$_3$, also influences the structural and optical properties of ZnGa$_2$O$_4$ phosphor. Excess ZnO has limit solubility in ZnGa$_2$O$_4$ phosphor whereas excess Ga$_2$O$_3$ is insoluble in ZnGa$_2$O$_4$ phosphor. Also, the presence of Zn vacancies in the phosphor system causes a blueshift in the luminescent emission.

Kim et al. [93] reported that the color of the emission oscillated between ultraviolet (360 nm) and blue (430 nm) by reduction (hydrogen ambient) and oxidation (air ambient), respectively. This ultraviolet luminescence was first considered to originate from the optical center related to gallium at the tetrahedral site in the host [83]. But Kim et al. [93] attributed the origin of the 360 nm emission to the Ga-O transition at distorted octahedral sites due to the
presence of oxygen vacancies ($V_o^*$) in ZnGa$_2$O$_4$ in the reducing ambient and the 430 nm emission to the Ga-O transition at regular octahedral sites without $V_o^*$ presence. His arguments were very well supported by electron paramagnetic resonance (EPR) experiments and x-ray photoelectron spectroscopic (XPS) studies. He also observed the 680 nm emission in reduced ZnGa$_2$O$_4$ arising from oxygen vacancies.

ZnGa$_2$O$_4$ can be made to emit in the different regions of the visible spectrum by suitably doping it with transition metals or rare-earth elements. Mn$^{2+}$ activated ZnGa$_2$O$_4$ has been widely investigated as an efficient green emitting phosphor [87]. The material emits green even when doped with Tb [94] or Tm. Activation with Co [95], Cr and Eu [96, 97] gives red and by Ce gives blue. There are reports stating that a systematic tuning (usually, a redshift) of the luminescent properties of self-activated ZnGa$_2$O$_4$ phosphors is possible by Cd [98] or Si [99] substitution.

Zinc gallate powder phosphors are synthesized by the conventional solid state reaction method which employs high temperature firing (> 1200°C) for highly extended heating times (~ 12 hrs) [88]. Several chemical methods have also been proposed to yield doped and undoped ZnGa$_2$O$_4$ phosphor particles with improved morphology and luminescent performance. Some of them are multistage precipitation method [100], microencapsulation method [101], combustion synthesis [102], co-precipitation of metal salts [103], aerosol pyrolysis [104] and spray pyrolysis [105] techniques. Citrate-gel [97] and sol-gel [106] techniques have been used in synthesizing zinc gallate phosphors with
high homogeneity and crystallinity at low temperatures. The identification of organic precursors [107] with specific and controlled properties that could finally yield transparent ZnGa$_2$O$_4$ coatings has also been reported.

Thin films of doped and undoped ZnGa$_2$O$_4$ are usually deposited by rf magnetron sputtering and pulsed laser ablation techniques. Films are also being deposited using electrophoresis [108] and plasma enhanced chemical vapor deposition (PECVD) [109].

The choice of the substrate had a profound influence on the structural and luminescent properties of ZnGa$_2$O$_4$ thin film phosphor. The luminescence of the doped or undoped sputtered ZnGa$_2$O$_4$ thin films improved when deposited on ITO coated glass substrates than on amorphous or Si substrates [110]. As compared to randomly oriented polycrystalline deposits on glass substrates, pulsed laser deposited thin films grown on single crystalline substrates - Si (100), Al$_2$O$_3$ (0001) and MgO (100) - gave better luminescence even without post-deposition annealing [111, 112]. This, in fact, reflected the adverse effect of grain boundaries on luminescence properties and suggested that lower defect densities result when films are grown on low energy surfaces. These works also proposed that MgO (100) served as a promising substrate for high quality ZnGa$_2$O$_4$ film growth.

The crystallinity, morphology and luminescent characteristics of the thin films were found to be highly sensitive to the substrate temperature, Zn/Ga ratio, ambient gas (oxygen) pressure and the temperature and atmosphere chosen for
post-deposition treatments. The films deposited at substrate temperatures ≥ 500°C with (311) spinel peaks showed excellent luminescent performance irrespective of the deposition technique chosen. Slightly Zn deficient films were found to exhibit better luminescent response in comparison to stoichiometric films. Zn/Ga stoichiometry can further be controlled by using mosaic ZnGa₂O₄/ZnO ablation targets to compensate for the Zn loss during deposition. The microstructural characteristics of sputter deposited ZnGa₂O₄:Mn thin films were also influenced by the energetic particle bombardment on varying the oxygen partial pressure [113]. Post-deposition annealing improved the crystallinity and inturn the luminescent properties of the as-deposited films [114]. The presence of a ZnO [115] or In₂O₃ [116] buffer layer also improved the crystallinity of the as-deposited sputtered films and inturn influence its luminous properties. The incorporation of S [117] and Se [118], as in the bulk, was reported to enhance the PL output of Mn doped zinc gallate thin film phosphors compared to the undoped material by a factor > 3. The addition of Li also was found to enhance the PL and CL properties of undoped and Mn doped ZnGa₂O₄ [119].

ZnGa₂O₄ has been demonstrated as an excellent host material for multicolor emitting phosphor layers in ACTFEL devices [120]. Minami and his group have fabricated ZnGa₂O₄:Mn active ACTFEL devices using the single insulating layered structure. The phosphor layers were sputter deposited onto thick ceramic sheets of BaTiO₃. 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 [120-122] or subjected to insitu RTA (rapid thermal
annealing) [123] to improve their performance. These devices gave a green EL emission with luminance over 600 cd/m² and an efficiency approaching 1 lm/W when driven at 1 KHz. Devices were also fabricated using low pressure chemical vapor deposition [100] and dip-coating [124] techniques for depositing the light emitting layers. Flynn et al. [125] has reported TFEL studies of ZnGa₂O₄: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 ZnGa₂O₄ as the active layer with luminescent efficiency approaching 15 (13) lm/W [126, 127].

White luminescence have been reported in Li doped ZnGa₂O₄ for the composition [0.9ZnGa₂O₄ + 0.1LiGaO₂], the chromaticity coordinates being (0.25, 0.34) [128]. Bismuth ion doped lithium zinc gallate (ZnGa₂O₄:0.001Bi³⁺, 0.175Li⁺) [129] also gives white emission with color coordinates (0.31, 0.33). Yang et al. [130] reports on the luminescence properties of a white ZnGa₂O₄/ZnO/ITO/glass phosphor screen deposited via sputtering.

Being an oxygen deficient spinel, ZnGa₂O₄ system has been studied to design a liquid petroleum gas sensor with high selectivity and sensitivity [131]. Recently, Risbud et al. [132] reported that a long range ferromagnetic order can be observed in Fe doped ZnGa₂O₄ at a relatively high temperature of 200 K. Long period phosphorescence has also been reported in ZnGa₂O₄:Mn phosphors [133]. ZnGa₂O₄: Mn²⁺, a well known green emitter, is widely used in cathode ray tubes, image intensifiers, television screens, etc. Zinc gallate phosphors have gained much attention for use in VFDs and FEDs, being an efficient low voltage
cathodoluminescent (LVCL) phosphor. The cubic spinel ZnGa$_2$O$_4$ therefore shows excellent potential for incorporation in future display systems.

### 1.8. Relevance of the present work

There is a continuing potential for commercialization of spinel oxide phosphors. In the present work, attempts are made to reduce the processing temperature of ZnGa$_2$O$_4$ so that the relatively inexpensive glass substrates and plastics can, in future, be used in ACTFEL device fabrication. Also, a novel white phosphor system - singly activated ZnGa$_2$O$_4$ - was investigated since the identification of new multicolor or white light emitting phosphor materials is a major challenge in the area of FPD technology.

### References


Chapter 1


