CHAPTER TWO

Experimental Techniques and Characterization tools

2.1 Introduction

Any solid or liquid object with one of its dimensions very much less than that of the other two may be called a ‘thin film’ [1]. Thin film devices would typically be about 5 to 50 μm thick in contrast to bulk devices, which are about 50 to 250 μm thick [2]. If the growth is atom by atom or molecule by molecule it is called thin film and if the growth is grain by grain it is thick film. A wide variety of microstructures and consequently properties can be obtained by simply varying the deposition conditions during the growth of the film. Thin film properties are strongly dependent on the methods of deposition, the substrate materials, the substrate temperature, the rate of deposition and the background pressure. The application and the properties of the given material determine the most suitable technique for the preparation of thin films of that material.

The thin films prepared for the studies presented in this thesis were mainly deposited using electron beam evaporation and thermal evaporation techniques. The structural, optical and electrical properties of these films, bulk and nanophosphor samples were studied using different characterisation tools.

2.2 Thin film deposition Techniques

Generally any thin film deposition follows the sequential steps: a source material is converted into the vapour form (atomic/molecular/ionic species) from the condensed phase (solid or liquid), which is transported to the substrate and then it is allowed to condense on the substrate surface to form
the solid film [2]. Depending on how the atoms/molecules/ions/clusters of species are created for the condensation process, the deposition techniques are broadly classified into two categories, viz. physical methods and chemical methods.

Chemical bath deposition, chemical vapour deposition, and spray pyrolysis are examples of chemical method of thin film deposition. Thermal evaporation, e beam evaporation, rf and dc sputtering and pulsed laser deposition (PLD) are examples of physical methods of thin film preparation.

The following sections discuss the methodology and experimental set-up used in various thin film deposition techniques.

### 2.2.1 Thermal evaporation by resistive heating

Thermal evaporation is the most widely used technique for the preparation of thin films of metals, alloys, and also many compounds, as it is very simple and convenient. Here the only requirement is to have a vacuum environment in which sufficient amount of heat is given to the evaporants to attain the vapour pressure necessary for the evaporation. The evaporated material is allowed to condense on a substrate kept at a suitable temperature.

When evaporation is made in vacuum, the evaporation temperature will be considerably lowered and the formation of the oxides and incorporation of impurities in the growing layer will be reduced. Evaporation is normally done at a pressure of $10^{-5}$ Torr. At this pressure a straight line path for most of the emitted vapour atoms is ensured for a substrate to source distance of nearly 10 to 50 cm [3]. The characteristics and quality of the deposited film will depend on the substrate temperature, rate of deposition, ambient pressure, etc. and the uniformity of the film depends on the geometry of the evaporation source and its distance from the source. The deposition by
thermal evaporation is simple, convenient and is widely used. Excellent and detailed reviews on the know-how of the thermal evaporation have been discussed by Holland [4].

2.2.2 Electron-Beam Evaporation Method

The evaporation technique is useful for non-refractory materials that will vapourise at a reasonable temperature, less than $1400^0 \text{C}$ for thermal sources and less than $2200^0 \text{C}$ for electron-beam sources. Typically, evaporation can produce good film stoichiometry for elements and simple compounds. Specifically, the evaporation technique has difficulty producing good films of complex phosphors like rare earth oxysulphides because of the widely components of these compounds. On the other hand, the classical II-VI compounds form excellent films by evaporation [5].

![SrS evaporation kinetics](image)

Figure 2.1 SrS evaporation kinetics
The kinetics of the evaporation, material transport and film condensation are shown in figure 2.1. The strength of the chemical bonding in these compounds are weak enough that the heat of evaporation is sufficient to largely dissociate the molecule. The individual atomic species are then transported to the substrate in a line of sight trajectory provided that the pressure level is low enough to permit collisionless transport. The atoms then recombine on the substrate to form II-VI compound. A feature of this recombination at the substrate is that it can be controlled to produce very stoichiometric films by adjusting the substrate temperature. The mechanism here is that the vapour pressure of the constituent atoms, for example Sr and S, is high enough for high substrate temperatures that neither Sr nor S atoms will adhere to other similar atoms. Thus film growth proceeds by formation of alternate layers of Sr and S atoms and stoichiometry is automatically achieved.

The simple resistive heating of an evaporation source suffers from the disadvantages of possible contamination from the support material and the limitations of input power, which make it difficult to evaporate high melting point materials.
These drawbacks may be overcome by an efficient source of heating by electron bombardment of the material. In principle, this type of source is capable of evaporating any material at rates ranging from fractions of an angstrom to microns per second. Thermal decomposition and structural changes of some chemical compounds may occur because of the intense heat and energetic electron bombardment.

The electron beam gun (figure 2.2) fits in the vacuum chamber which consists of a W filament, anode, permanent magnet etc. It is operated by a high voltage power supply (3kW). When it is operated the W filament is heated by the low tension until it becomes incandescent and then emits electrons spontaneously and randomly. The anode plate then collects the electrons and forms them into a beam which is accelerated through the high voltage potential of 6kV. (figure 2.3). Magnetic fields created by a permanent magnet and the pole pieces and pole piece extensions deflect the beam.
through 270° until it impacts on the evaporant in the crucible hearth which is at electrical ground potential.

![Diagram of electron beam gun](image)

**Figure 2.3 Principle of operation of electron beam gun.**

A schematic diagram of the electron beam evaporation system is shown in figure 2.4.

The combined force, \( F \), on an electron in electric and magnetic fields known as Lorentz force is given by

\[
F = F_E + F_B = q_eE + q_e(v \times B)
\]

The second force is balanced by the centrifugal force of the electrons curving at radius \( r \), that is

\[
|q_e v \times B| = m|v^2|/r
\]
Thus the "cyclotron" or "Larmor" radius of an electron orbiting in a magnetic field is

\[ r = \frac{m_e v_\perp}{q_e |B|} \]

Where \( v_\perp \) is the component of \( v \) perpendicular to \( B \).

The electron beam instead of hitting a single point can be made to move in \( X \) and \( Y \) directions using a pair of horizontally and vertically deflecting sweep coils.
The source material is contained by a Cu hearth which is water-cooled to prevent it's outgassing or melting. Cooling also prevents the hearth from alloying with molten source materials. Then the source material is evaporated from a crucible. A schematic representation of electron beam evaporation system is shown in figure 2.4

This evaporation technique done with narrow intense energy beam is subject to “macroparticle-spitting” problem. One mechanism of macroparticle ejection common to all vaporization methods and dominant for electron beams is the sudden evaporation of a nodule of a particular contaminant whose vapour pressure is much higher than that of the source material. The volatile contaminant nodule which ejects the macroparticle may be an inclusion in the solid source material, a gaspocket trapped within sintered material, or a slag accumulating on the surface of molten metal by reaction background gases with the metal or by precipitation of bulk contaminants upon melting the metal.

Although electron-beam evaporation is a thermal process, so that the vapour atoms leave the surface with only thermal energy of ~0.2eV, several kinds of non thermal energy still arrive at the film surface. One is x-rays generated by electron-beam impact on the source material. But they are not hard enough to penetrate the vacuum chamber wall or window to become a hazard to the operator [6]. The second form of non thermal energy accompanying electron-beam evaporation is positive ions generated above the source by impact of the incoming beam upon the outgoing vapour. Sometimes a gaseous source species is introduced into the evaporation chamber for the purpose of forming a compound film by reaction with the evaporating species.
2.3 Characterisation tools

The optimisation of the preparation conditions is the main task in order to get device quality phosphor material. This has to be carried out on the basis of detailed study on structural, compositional, morphological, optical and electrical properties of the film and bulk phosphors obtained at different growth conditions. In the following sections the techniques used for the film characterizations are discussed briefly.

2.3.1 Thin film thickness

Thickness plays an important role in the film properties unlike a bulk material. Reproducible properties are achieved only when the film thickness and the deposition parameters are kept constant. Film thickness may be measured either by in-situ monitoring of the rate of deposition or after the film deposition. The thicknesses of the thin films prepared for the work presented in this thesis were measured by a stylus profiler (Dektak 6M).

The stylus profiler takes measurements electromechanically by moving the sample beneath a diamond tipped stylus. The high precision stage of this equipment moves the sample according to a user defined scan length, speed and stylus force. The stylus is mechanically coupled to the core of a linear variable differential transformer (LVDT). The stylus moves over the sample surface. Surface variations cause the stylus to be translated vertically. Electrical signals corresponding to the stylus movement are produced as the core position of the LVDT changes. The LVDT scales an ac reference signal proportional to the position change, which in turn is conditioned and converted to a digital format through a high precision, integrating, analog-to-digital converter [7]. The film whose thickness has to be measured is
deposited by masking a small region which creates a step on the sample surface. The thickness of the sample can be measured accurately by measuring the vertical motion of the stylus over the step.

2.3.2 X-ray diffraction studies

Electrical and optical properties of a substance are influenced by their crystallographic nature. X-ray diffraction (XRD) studies were carried out to understand the crystallographic properties of the phosphors prepared. A given substance always produces a characteristic x-ray diffraction pattern whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. The particular advantage of x-ray diffraction analysis is that it discloses the presence of a substance and not in terms of its constituent chemical elements. Diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis the diffraction method has the advantage that it is much faster, requires only very small sample and is non destructive [8,9].

The basic law involved in the diffraction method of structural analysis is the Bragg's law. When monochromatic x-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal lattice acts as series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of $\lambda$. This condition is called Bragg's law and is given by the relation,

$$2d\sin\theta = n\lambda$$
where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of the x-rays, \( d \) is the spacing between consecutive parallel planes and \( \theta \) is the glancing angle (or the complement of the angle of incidence) [10].

X-ray diffraction studies gives a whole range of information about the crystal structure, orientation, average crystalline size and stress in the films. Experimentally obtained diffraction patterns of the sample are compared with the standard powder diffraction files published by the Joint Committee on Powder Diffraction Standards (JCPDS).

The average grain size of the film can be calculated using the Scherrer's formula [8],

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

where, \( \lambda \) is the wavelength of the x-ray and \( \beta \) is the full width at half maximum intensity in radians.

The lattice parameter values for different crystallographic systems can be calculated from the following equations using the (hkl) parameters and the interplanar spacing \( d \).

**Cubic system,**

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

**Tetragonal system,**

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]

**Hexagonal system,**

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]
X-ray diffraction measurements of the films in the present studies were done using Rigaku automated x-ray diffractometer. The filtered copper Kα (λ=1.5418Å) radiation was used for recording the diffraction pattern.

2.3.3 Atomic Force Microscopy (AFM)

Following the invention of the scanning tunnelling microscope (STM), a number of new scanning probe microscopes (SPM) has been developed that use the key components of the STM. One of the most important SPM is the atomic force microscope (AFM) [11,12]. In atomic force microscopy a tip, integrated to the end of a spring cantilever, is brought within the interatomic separations of a surface, such that the atoms of the tip and the surface are influenced by interatomic potentials. As the tip is rastered across the surface, it bounces up and down on the contours of the surface. By measuring the displacement of the tip (i.e. the deflection of the cantilever), one can theoretically map out the surface topography with atomic resolution. The first generation AFM measured cantilever deflections using a piggy-backed STM. Later instruments used more practical optical techniques. The AFM is essentially identical in concept to the scanning profilometer, except that the deflection-sensitivity and resolution are improved by several orders of magnitude. There are a large number of applications for the AFM, including biological systems, polymers, and a host of insulator and semiconductor materials.
Figure 2.5 The essential elements of an AFM

An AFM images a surface in a manner analogous to the gramophone stylus sensing the groves of gramophone disk. The essential elements of an AFM are shown in the figure 2.5. The tip is attached to a cantilever type spring. As the tip and sample interact, forces act on the tip and cause the cantilever (spring) to deflect. The cantilever position is monitored by a position detector. The output of the detector is connected to a feedback controller that regulates the force between the sample and the tip by moving the sample up or down. The sample is moved by a PZT scanning actuator. The cantilever must be soft enough to deflect a measurable amount without damaging the surface features of the sample. The amount of deflection is proportional to the force acting on the tip.

\[ F_{\text{spring}} = -k \cdot \Delta Z \]

where \( F \) is the force on the sample, \( k \) is the spring constant of the cantilever, and \( \Delta Z \) is the deflection of the cantilever.
Various modes of AFM measurements include contact mode, dynamic force mode, phase mode. Friction force microscope, magnetic force microscope, surface potential microscope, etc are scanning probe microscopes with slight variation in the working principles from that described above.

2.3.4 Transmission spectroscopy

Intrinsic optical absorption of a single photon across the band gap is the dominant optical absorption process in a semiconductor. When the energy of the incident photon (\(h\nu\)) is larger than the band gap energy the excitation of electrons from the valence band to the empty states of the conduction band occurs. The light passing through the material is then absorbed and the number of electron hole pairs generated depends on the number of incident photons \(S_0(\nu)\) (per unit area, unit time and unit energy). The frequency \(\nu\) is related to the wavelength \(\lambda\) by the relation, \(\lambda = \frac{c}{\nu}\), where \(c\) is the velocity of light. The photon flux \(S(x,\nu)\) decreases exponentially inside the crystal according to the relation [13],

\[
S(x,\nu) = S_0(\nu) \exp(-\alpha x)
\]

where, the absorption coefficient \(\alpha\), \((\alpha(\nu) = \frac{4\pi k\nu}{c})\) is determined by the absorption process in semiconductors and \(k\) is the extinction coefficient.

For the parabolic band structure, the relation between the absorption coefficient \((\alpha)\) and the band gap of the material is given by [13],

\[
\alpha = \frac{A}{h\nu} (h\nu - E_g)^r
\]
where, \( r = 1/2 \) for allowed direct transitions, \( r = 2 \) for allowed indirect transitions, \( r = 3 \) for forbidden indirect transitions and \( r = 3/2 \) for forbidden direct transitions. \( A \) is the parameter which depends on the transition probability. The absorption coefficient can be deduced from the absorption or transmission spectra using the relation,

\[
I = I_0 e^{-\alpha t}
\]

where, \( I \) is the transmitted intensity and \( I_0 \) is the incident intensity of the light and \( t \) is the thickness of the film. In the case of direct transition, from equation \((\alpha \Delta v)^2\) will show a linear dependence on the photon energy \((\Delta v)\). In the case of direct bandgap semiconductor a plot of \((\alpha \Delta v)^2\) against \(\Delta v\) will be a straight line and the intercept on energy axis at \((\alpha \Delta v)^2\) equal to zero will give the band gap energy.

The transmissions of the thin films were recorded using Hitachi uv-vis-nir 330 spectrophotometer and Jasco V500 spectrophotometer.

2.3.5 Diffuse reflectance spectroscopy

The measurement of radiation reflected from a surface constitutes the area of spectroscopy known as diffuse reflectance spectroscopy (DRS). Diffuse reflectance spectrometry concerns one of the two components of reflected radiation from an irradiated sample, namely specular reflected radiation, \( R \) and diffusely reflected radiation, \( R_{\text{diff}} \). The former component is due to the reflection at the surface of single crystallites while the latter arises from the radiation penetrating into the interior of the solid and re-emerging to the surface after being scattered numerous times. These spectra can exhibit both absorbance and reflectance features due to contributions from transmission,
internal and specular reflectance components as well as scattering phenomena in the collected radiation.

Based on the optical properties of the sample, several models have been proposed to describe the diffuse reflectance phenomena. The Kubelka-Munk model put forward in 1931 is widely used and accepted in diffuse reflectance infrared spectrometry.

The intensity of the reflected light depends on the scattering coefficient \( s \) and the absorption coefficient \( k \). The reflectance data can be converted to absorbance by Kubelka-Munk equation [14,15].

Kubelka-Munk equation is as

\[
\log \left( \frac{1 - r_{\infty}}{2 r_{\infty}} \right) = \log k - \log s
\]

Where \( r_{\infty} = R_{\infty}(\text{sample})/ R_{\infty}(\text{standard}) \). Here the standard used is MgO. \( R_{\infty}(\text{standard}) \) is taken as unity. \( R_{\infty}(\text{sample}) \) is the diffuse reflectance of the sample \( (R = I_{\text{sample}}/I_{\text{ref}}) \).

\[
(1 - R)^2 / 2 R = k/s
\]

The band gap is estimated from the plot of \( \{(k/s) \cdot h\nu\}^2 \) versus \( h\nu \), and extrapolating the graph to the X axis.

2.3.6 Photoluminescence (PL) measurements

Two types of luminescence spectra can be distinguished: excitation and emission. In the case of an excitation spectrum the wavelength of the
exciting light is varied and the intensity of the emitted light at a fixed emission wavelength is measured as a function of the excitation wavelength. The excitation spectrum gives information on the position of excited states just as the absorption spectrum does, except that the former reveals only the absorption bands that result in the emission of light. The observed differences between the absorption and excitation spectra can yield useful information. An emission spectrum provides information on the spectral distribution of the light emitted by a sample. The time resolved PL measurements are a powerful tool for the determination of the radiative efficiency. The radiative efficiency specifies the fraction of excited states, which de-excite by emitting photons. The PL studies give information on the effect of doping in phosphors. Luminescence decay indicates the defect density in the film sample by comparing the normalized area under the decay curve of the powder samples when non-radiative de-excitation occurs [16].

The emission and excitation spectra for the powder and thin film samples are recorded using Fluoromax-3 spectrofluorimeter. The FluoroMax-3 is a spectrofluorimeter from JY-Horiba that is applicable to fluorescent intensity measurements. The fluorimeter follows a classical configuration with a Xenon arc lamp, excitation and emission monochromators, a photomultiplier tube (PMT) for detection and a reference photodiode. The Xenon lamp supplies a wide range of excitation light but to perform high resolution fluorescence measurements discrete wavelengths of light must be employed. Wavelength selection is achieved by the optical gratings of the monochromators which diffract incident light, dispersing it into its constituent wavelength components. In addition, adjustable 'slits' form the entrance and exits of monochromators and these components further resolve light wavelengths. On the excitation monochromator the slits control the bandpass (range) of light that is incident on the sample whereas the slits of
the emission monochromator determine the intensity of the emitted fluorescence recorded by the PMT. Finally, the reference photodiode is employed to correct for variations in the emission intensity of the Xenon lamp that occur at different wavelengths. As such, the FluoroMax-3 is a serious piece of equipment capable of performing high-resolution and sensitive fluorescence measurements. Further, provision for sample temperature control and stirring mean that this fluorimeter can also be used for cell biological applications in addition to basic solution studies.

2.3.7 CIE color Coordinates

In 1931, the commission Internationale de l’Eclairage (CIE) established an international standard for quantifying all visible colors, known as CIE color coordinates. The CIE has defined a system that classifies color according to the HVS (the human visual system). Using this system we can specify any color in terms of its CIE coordinates. The CIE system works by weighting the SPD (spectral power density) of an object in terms of three-color matching functions. These functions are the sensitivities of a standard observer to light of different wavelengths. The weighting is performed over the visual spectrum, from around 360nm to 830nm in set intervals. However, the illuminant, and lighting and viewing geometry are carefully defined, since these all affect the appearance of a particular color. This process produces three CIE tri-stimulus values, XYZ, which are the building blocks from which many color measurements are made.

Any color can be described as a mixture of three primary colors or "Tristimuli", typically RGB for CRT based systems (TV, computer) or XYZ (fundamental measurements). The amounts of each stimulus define the color.
The CIE coordinates are obtained by computing the three CIE tristimulus values, X, Y and Z and subsequently computing the CIE coordinates x and y from these values. The CIE tristimulus values are obtained by integrating the product of the spectrum of the light source P(λ), and CIE color matching functions, x_λ(λ), y_λ(λ) and z_λ(λ) as shown in figure 2.6 [17].

Since the spectra are measured as discrete values, integration is replaced by sum given as,

\[
X = \Delta \lambda \sum x_\lambda(\lambda) P_\lambda(\lambda) \\
Y = \Delta \lambda \sum y_\lambda(\lambda) P_\lambda(\lambda) \\
Z = \Delta \lambda \sum z_\lambda(\lambda) P_\lambda(\lambda)
\]

Figure 2.6. The CIE color matching function for CIE 1931 standard observer.
Where $\Delta \lambda$ is the interval between the points. The CIE is calculated from the above values using the equations:

\[
x = \frac{X}{X+Y+Z}
\]
\[
y = \frac{Y}{X+Y+Z}
\]
\[
z = \frac{Z}{X+Y+Z}
\]

However, because,

$x + y + z = 1$; only two of the three CIE color coordinates are independent. Hence only $x$ and $y$ values are reported. Plotting of the CIE $y$ color coordinates versus the CIE $x$ color coordinate over the visual range of light leads to a horseshoe shaped diagram known as the CIE chromaticity diagram represented in figure 2.7.

The dot at the center represents white light. CIE coordinates corresponding to red, green, blue and white light is given in table 2.1. When the CIE coordinate of a color are specified, the dominant wavelength of the color is the intersection of the line connecting these CIE coordinates and those of white light with the upper arc of the diagram. Further, when the light emission from phosphors of two colors is mixed, the range of colors that it is possible to produce by mixing these colors is given by the line that ties the CIE coordinates of these two colors together [18].
The CIE color coordinates are most useful for the optical characterization of phosphors as guidelines to gauge the quantity of the chromaticity available from a full color display. The CIE coordinates are thus a powerful concept, which represent an entire luminescent spectrum by two numbers.

Table 2.1. CIE coordinates for phosphors in trichromatic system

<table>
<thead>
<tr>
<th></th>
<th>Red</th>
<th>Green</th>
<th>Blue</th>
<th>White</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>0.65</td>
<td>0.3</td>
<td>0.15</td>
<td>0.33</td>
</tr>
<tr>
<td>y</td>
<td>0.35</td>
<td>0.6</td>
<td>0.1</td>
<td>0.33</td>
</tr>
</tbody>
</table>
2.3.8 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as the specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% O₂ in N₂ or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry, or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process. In the particular case of carbon nanotubes, the weight change in an air atmosphere is typically a superposition of the weight loss due to oxidation of carbon into gaseous carbon dioxide and the weight gain due to oxidation of residual metal catalyst into solid oxides.

TGA instruments can be divided into two general types: vertical and horizontal balance. Vertical balance instruments have a specimen pan hanging from the balance (TA Instruments, etc) or located above the balance on a sample stem (Netzsch). It is necessary to calibrate these instruments in order to compensate for buoyancy effects due to the variation in the density of the purge gas with temperature, as well as the type of gas. Vertical balance instruments generally do not have reference pan and are incapable of true DTA or DSC measurements (Netzsch being an exception). Horizontal
balance instruments (TA, Perkin Elmer, etc.) normally have two pans (sample and reference) and can perform DTA and DSC measurements. They are considered free from buoyancy effects, but require calibration to compensate for differential thermal expansion of balance arms. Applications of the TG/DTA instrument are compositional analysis, decomposition temperature, oil volatility measurements, flammability studies, heat of transition, thermal stability analysis, oxidative stability analysis, transition temperature detection etc. In the present study TGA was performed using Perkin Elmer, Diamond TG/DTA

2.3.9 Inductively Coupled Plasma- Atomic Emission Spectroscopy

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is one of several techniques available in analytical atomic spectroscopy for compositional analysis. ICP-AES utilizes a plasma as the atomization and excitation source. A plasma is an electrically neutral, highly ionized gas that consists of ions, electrons, and atoms. The energy that maintains an analytical plasma is derived from an electric or magnetic field. Most analytical plasmas operate with pure argon or helium, which makes combustion impossible. Plasmas are characterized by their temperature, as well as their electron and ion densities. Analytical plasmas typically range in temperature from 600 to 8,000 K. As a comparison, the temperature of the sun’s interior is millions of degrees, while its surface temperature is approximately 10,000 K.

The steps involved in determining the elemental content of an aqueous phase sample by ICPAES are: [19]

1. Sample Preparation: Some samples require special preparation steps including treatment with acids, heating, and microwave digestion.
2. Nebulization: Liquid converted to aerosol.
3. Atomization: Gas phase bonds are broken, and only atoms are present. Plasma temperature and inert chemical environment are important at this stage.
4. Desolvation/Volatization: Water is driven off, and remaining solid and liquid portions are converted to gases.
5. Excitation/Emission: Atoms gain energy from collisions and emit light of a characteristic wavelength.

The atomic spectrum emitted by a sample is used to determine its elemental composition in this instrument. The wavelength at which emission occurs identifies the element, while the intensity of the emitted radiation quantifies its concentration. Thermo Electron IRIS INTREPID II XSP DUO was used for the determination of elemental composition in the phosphors.

2.3.10 Electron Paramagnetic Resonance (EPR) spectroscopy

Electron Paramagnetic Resonance (EPR) spectroscopy, often called Electron Spin resonance (ESR) spectroscopy is based on the absorption of microwave radiation by an unpaired electron when it is exposed to a strong magnetic field. Species that contain unpaired electrons (namely free radicals, odd-electron molecules, transition metal complexes, rare earth ions, etc.) can therefore be detected by EPR. Qualitative and quantitative estimation of compounds can be made by EPR. It is widely used as a non-destructive technique in determining the structure of transition metal complexes and organic free radicals.
Zavoisky discovered electron paramagnetic resonance (EPR) which is also called as electron spin resonance (ESR) in 1944 in USSR. He observed the first EPR spectrum in CuCl$_2$.2H$_2$O in 1945. The EPR technique is an extension of Stern-Gerlach experiment.

When a sample is subjected to static magnetic field, the interaction between the magnetic moment of the electron and applied magnetic field splits the Zeeman energy levels. Application of microwave radiation perpendicular to the magnetic field causes excitation of electrons from one level to the other. The resulting absorption of the microwave is modulated to record first derivative of the absorption. Conventionally EPR spectra are recorded as first derivative rather than absorption to improve the resolution. In fact, second derivatives are also recorded when necessary.

The electron magnetic moment is coupled with the nuclei that it is associated with. Most nuclei and their isotopes have a magnetic moments characteristic of them. The electron magnetic moment interacts with the nuclear magnetic moment. This results in further splitting of Zeeman energy levels which appears as multiple lines in the spectrum.

When the system has more than one unpaired electron, the energy levels are split even in the absence of applied magnetic field due to the interaction between the electrons. It is known as the zero-field splitting. The number of splitting of the energy levels is given by $(2S+1)$, where $S$ is the total spin of the electron. The nuclear hyperfine splitting is given by $(2I+1)$ where $I$ is the nuclear spin quantum number [20-22].

In general, EPR spectroscopy deals with the paramagnetic compounds to study the magnetic properties of the materials. EPR spectrometer generally operates at a constant frequency while magnetic field is swept. Many models
of EPR instruments are built to operate at several frequencies ranging from 250 MHz to 100 GHz. Popular models operate at 9.5 and 35 GHz called as X- and Q-band frequencies (the names X and Q are historical whose origin comes from the application of microwaves to military). At these frequencies, the energy of the radiation is 0.3 and 1.0 wavenumbers. This allows one to study the transitions of the order of 0.00001 cm⁻¹ which makes this technique extremely powerful in studying weak interactions. Hyperfine couplings, intermolecular interactions like exchange coupling, etc. reveal very useful information about the structure and the magnetic properties of the molecule. The technique is very sensitive and it is possible to detect sub-micromolar quantities of paramagnetic species.

Varian E-112 spectrometer generates microwave from klystron, suitably attenuates and allows it to pass through a circulator to a reflection type cavity (figure 2.8). The change in the microwave flux in the cavity during resonance absorption is detected using a crystal detector. The microwave frequency is detected using a crystal detector. The microwave frequency is modulated with a 100 kHz field and the output from the crystal detector is phase detected and amplified, thus providing a first derivative of absorption as a function of magnetic field.
2.3.11 Transmission Electron Microscopy (TEM).

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film or to be detected by a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and James Hillier at the university of Toronto in 1938 using concepts developed earlier by Max Knoll and Ernst Ruska.
Like all matter, electrons have both wave and particle properties (as theorized by Louis-Victor de Broglie), and their wave-like properties mean that a beam of electrons can in some circumstances be made to behave like a beam of radiation. The wavelength is dependent on their energy, and so can be tuned by adjustment of accelerating fields, and can be much smaller than that of light, yet they can still interact with the sample due to their electrical charge. Electrons are generated by a process known as thermionic discharge in the same manner as the cathode in a cathode ray tube, or by field emission; they are then accelerated by an electric field and focused by electrical and magnetic fields onto the sample. The electrons can be focused onto the sample providing a resolution far better than is possible with light microscopes, and with improved depth of vision. Details of a sample can be enhanced in light microscopy by the use of stains; similarly with electron microscopy, compounds of heavy metals such as osmium or lead or uranium can be used to selectively deposit heavy atoms in the sample and enhance structural detail, the dense nuclei of the heavy atoms scatter the electrons out of the optical path. The electrons that remain in the beam can be detected using a photographic film, or fluorescent screen among other technologies. So areas where electrons are scattered appear dark on the screen, or on a positive image[11].

In the most powerful diffraction contrast TEM instruments, crystal structure can also be investigated by High Resolution Transmission Electron Microscopy (HRTEM), also known as phase contrast imaging as the images are formed due to differences in phase of electron waves scattered through a thin specimen.

Resolution of the HRTEM is limited by spherical and chromatic aberration, but a new generation of aberration correctors has been able to overcome
spherical aberration. Software correction of spherical aberration has allowed
the production of images with sufficient resolution to show carbon atoms in
diamond separated by only 0.89 angstroms and atoms in silicon at 0.78
angstroms (78 pm) at magnifications of 50 million times. Improved
resolution has also allowed the imaging of lighter atoms that scatter electrons
less efficiently — lithium atoms have been imaged in lithium battery
materials. The ability to determine the positions of atoms within materials
has made the HRTEM an indispensable tool for nanotechnology research
and development in many fields, including heterogeneous catalysis and the
development of semiconductor devices for electronics and photonics.

2.3.12 Resistivity by two probe method

The resistivity of the bulk sample can determined by the two-probe method.
Evaporated indium layers or high conducting silver paste is used as the
electrodes on two sides of the pelletised sample. The current voltage
measurements are carried out using a Keithley's source measure unit (Model
SMU 236). The resistivity (ρ) of the sample is calculated applying ohm’s
law, by the relation ρ = RA/L, where R is the resistance given by the slope
of the current – voltage characteristic curve, A is the cross sectional area and
L is the thickness of the pellet.

2.3.13 Luminance-Voltage (L-V) Characterization

The driving waveform used to operate an ACTFEL device can be a sine
wave, triangular wave or bipolar trapezoidal voltage waveform. The standard
bipolar waveform used for most of the electrical characterization techniques
consists of a 1 KHz sequence of bipolar trapezoidal pulses with rise and fall
times of 5 μs and a pulse width of 30 μs. It is to be noted that the polarity of
the applied voltage pulse is defined with respect to the top electrode (i.e. the electrode farthest away the substrate). The voltage values should be indicated in zero-to-peak values, rather than in rms values, since luminance depends on the peak voltage value. The pulse width, $\tau$, is defined by the full width at the half maximum of the actual (deformed) pulse drive waveform applied to an EL device, and the rise time $t_r$ and the fall time $t_f$ are defined by the time period corresponding to 10%-to-90% value and 90%-to-10% value, respectively, of the actual voltage. The recommended values for practical applications are $\tau = 40 \, \mu s$, $t_r \leq 8 \, \mu s$ and $t_f \leq 8 \, \mu s$ (figure 2.9).

![Diagram of pulse waveforms](image)

Figure 2.9. Driving waveform of an ACTFEL device

The most commonly used techniques to compare and contrast ACTFEL devices from an industrial viewpoint are measurements that explore its light output, the power required to generate that light and the color of light emitted. The optical response of an ACTFEL device to an electrical stimulus is critical in specifying the display performance.
Several important ACTFEL parameters, namely, the threshold voltage ($V_{th}$) and luminance at $V_{th} + 40\,\text{V}$ ($L_{40}$) can be determined from luminance versus voltage ($L$-$V$) measurements. The method requires a variable ac voltage supply (typically 0-300 V) and a spectrometer to measure the luminance as a function of the applied voltage. Luminance is measured varying the amplitude of the applied waveform. Once the data is collected, plotting voltages on the x-axis and the corresponding luminances on the y-axis gives the L-$V$ curve. A typical L-$V$ plot is shown in figure 2.10. This gives the luminous intensity output in a direction normal to the emitting surface, and is generally reported in either foot-Lamberts (ft-L) or candelas per square meter ($\text{cd/m}^2$) [$1\text{ft-L} = 3.426\,\text{cd/m}^2$].

The threshold voltage is typically defined to be the voltage where a luminance of 1 $\text{cd/m}^2$ is achieved. At this external voltage, the field inside the phosphor is high enough to cause electrons to excite the luminescent centers and generate light. As the voltage increases above threshold, the phosphor electric field increases proportionally, as does the electron energy distribution. Consequently, luminance sharply increases with voltage until the phosphor brightness saturates or until the phosphor layer experiences dielectric breakdown. The significance of the parameter $L_{40}$ is that most ACTFEL displays are driven at 40 V above threshold, which is the modulation voltage. When comparing $L_{40}$ values, it is important to consider both the threshold voltage and the frequency at which the device was driven. $L_{40}$ increases almost linearly with both phosphor thickness (i.e. $V_{th}$) and frequency. As thickness increases, there are more luminescent centers that electrons can excite; and when frequency increases, the number of passes that electrons make across the phosphor layer increases.
The L-V measurement is very sensitive to the nature of the driving waveform, driving voltage and its frequency. The measured luminance depends to some degree on the rise time, fall time and pulse width when bipolar trapezoidal waveforms are used to generate L-V data. The measured luminance at a fixed voltage increases quite noticeably with increasing frequency. This is because at higher frequencies, more pulses are applied to the ACTFEL device per unit time, hence, the luminescent impurities are excited more often. Unfortunately, there is a point of diminishing returns with increasing frequency where the luminance either saturates or decreases at a certain frequency. This effect has to do with both device heating and the de-excitation time of the luminescent impurities. Additionally, when the period of the driving waveform is of the same order as the characteristic decay time of the luminescent impurity, there may be little or no increase in
luminance with increasing frequency because many luminescent impurities may already be excited when the following pulse arrives. Essentially, the fraction of time per second that the driving waveform spends above the turn-on voltage determines the relative luminance of the device.

Besides the chemical composition, the thickness of the phosphor layer affects the observed luminance of the ACTFEL device. As the phosphor layer gets thicker (given a fixed doping concentration), a greater number of luminescent impurities are incorporated into the phosphor layer, and the carriers have a greater probability of impact excitation. Therefore, with all else being equal, ACTFEL devices with thicker phosphor layers will exhibit greater luminance than thinner devices.

The insulators affect the luminance characteristics of an ACTFEL device mainly through their effect on the voltage distribution through the device. An increase of insulator capacitance with respect to a fixed phosphor capacitance results in a greater percentage of the applied voltage being dropped across the phosphor layer, which leads to a lower threshold voltage. The two methods of increasing the insulator capacitance are to either decrease the thickness of the insulator layers or use an insulating material with larger dielectric constant.

The doping level of the luminescent impurity also is critical in determining the L-V characteristics of an ACTFEL device. At low dopant concentrations (≤ 1% for most phosphor materials), the observed luminance increases monotonically with increasing luminescent impurity concentration. Then, an optimum luminance is achieved, and the luminance declines with increasing luminescent impurity concentration above this doping level. This decline is
due to the disruption of phosphor crystallinity and the increased number of non-radiative transition paths that result from high luminescent impurity doping levels. Furthermore, at higher luminescent impurity doping levels, hysteresis in the L-V characteristics is sometimes observed.

In the present work, the fabricated devices were electrically excited using a 1.5 KHz trapezoidal waveform generated from a pulsed signal generator (Digilog Instruments Ltd.). The bipolar pulse train driving the device had a characteristic rise and fall time of 30 µs each and a stay time of 70 µs. A 0.32 m monochromator (Triax-320) coupled with Hamamatsu R928 photomultiplier tube was used to record the electroluminescent output from the fabricated device.
2.4 References

6. Thin-Film Deposition-principles and practice, Donald L. Smith