Chapter - 3

3.1. Phosphor Synthesis methods and Related Technology:
Phosphate compounds have been utilized as a host material in phosphors since many decades, due to their relatively low material cost, easy synthesis and reasonable stability in different applications. The $\text{PO}_4^{3-}$ group is optically inert anion. It is transparent throughout the visible and ultraviolet spectrum, up to about 1750 Å. This minimizes any contribution to the spectra from the host. Most of the rare earth activated phosphors are synthesized by solid state diffusion reaction between the raw materials at high temperature. The synthesis of a phosphor with reproducible efficiency and chromaticity requires careful control on the purity, stoichiometry and particle size of the starting raw materials. The fig. 3.1 gives the flow chart of general’s concept of phosphor synthesis process.

![Flow chart of phosphor synthesis process](chart.png)
3.1.1 Solid state reaction method:

a. Outline of synthesis process: Almost all the industrial phosphors are synthesized by solid-state reaction technique. Figure 1 shows the general concept of the synthesis process. First the high purity materials of the host crystal, activators and fluxes are blended, mixed and then fired in container. As the product obtained by firing is more or less sintered, it is crushed, milled and then sorted to remove coarse and excessively crushed particles. In some cases the product undergoes surface treatment.

b. Purification of raw materials: - As small amounts of impurities (iron) sometimes change phosphor characteristics drastically, hence raw materials must be purified very carefully. In the rare earth raw materials, separation of a single rare earth ion from the others is most important.

c. Host synthesis and activator introduction: - A phosphor is composed of a host crystal or matrix and a small amount of activator(s). There are two different kinds of reactions in phosphor synthesis. In the first one, activator ions are introduced into an existing host material. In the second, host material synthesis and activator incorporation proceed simultaneously during firing.

d. Raw material blend ratio: - Luminescence efficiency of the material depends on the stoichiometric ratio. Hence raw materials are blended in a ratio some times deviating considerably from the stoichiometric composition of the final product.

Mechanism of solid state reaction during firing: - The elementary process taking place during firing can be investigated by doing differential thermal analysis (DTA),
thermo gravimetric analysis (TGA), crystal structure identification by X-ray diffraction, microscopic observation and chemical analysis.

**f. Crucibles and atmospheres:** - In the phosphor industry, quartz and silicon carbide are the most frequently used container materials for firing phosphors. For phosphors requiring higher firing temperatures alumina crucibles are employed. Box type furnaces are common for small scale production. For large scale production tunnel-type, continuous furnaces are required. Firing is carried out either in air or in a controlled atmosphere. Phosphors activated with Ce$^{4+}$ and Eu$^{3+}$ ions can be fired in air, whereas phosphors activated with Ce$^{3+}$ and Eu$^{2+}$ ions are fired in a reducing atmosphere. Two methods are employed for controlled atmosphere one is, as the reducing gas, nitrogen containing several percent of hydrogen is most frequently used and second one is keeping the small crucible containing phosphor in a big crucible containing carbon. Firing temperature range from 900-1200ºC for phosphate phosphors, 1000-1300ºC for silicates, and 1200-1500ºC for aluminates is used.

**Fluxes:** - The purpose of firing is not only to cause solid-state reactions but also to form well crystallized particles with an appropriate average diameter. The substance added to the raw material mixture to help crystal growth is called a flux. Fluxes are usually compounds of alkali or alkaline earth metals having low melting points. The halides are most frequently used. The flux used plays a determining role in the particle growth process. Each flux influences the particle size and the shape in a different way. Therefore, a combination of fluxes is sometimes used to obtain products with desired morphology. Another important function of the flux is that it acts as a source of the co-activator. One more advantage of the use of flux is the firing temperature can be reduced. Generally, phosphates and borates do not need fluxes.

**h. Impurities and additives:** - The presence of some impurity ions reduces luminescence efficiency, sometimes to a very great extent. On the contrary, there are some additives that influence phosphor characteristics in a positive way. The kind and quantity of the ions that change phosphor characteristics differ from phosphor to phosphor.

**i. Particle size control:** - Practical phosphors must be prepared so that they can form a dense, pinhole-free coating on a substrate. This property is determined mainly by particle size distribution and surface treatment. In the case of fluorescent lamp phosphor, the optimum coating thickness is roughly proportional to its mean particle size. Therefore small particle size is advantageous for expensive phosphors. On the
other hand, due to fine particle size, luminescence efficiency tends to become lower. Phosphors having a small particle size and high efficiency would be most useful. Usually mean particle diameter around 3-8μm. The same rule applies for the cathodoluminescent phosphors. Usually mean particle diameters between 5-7μm. For X-ray intensifying screens, the particle size is determined by considering efficiency, picture resolution and picture quality. Usually mean particle diameters between 1-10μm.

The parameters that control the particle diameter in the phosphor preparation process are listed below

1. Particle size of raw materials
2. Fluxes
3. Firing conditions
4. Milling
5. Particle classification

j. Surface treatment: - Some phosphors, as fired, are poorly dispersive in slurry. To improve dispersion, surface treatment is required.

k. Weighing Balance: - The below figure shows the German made Citizen Company five digit weighing balance having an accuracy of 0.01mg. All the samples were weighed using this balance.

Fig.3.1.1a Weighing Balance
After weighing the required compounds, since we are preparing the samples using solid state method, in order to diffuse into one another, two important steps to be done carefully.

1. Grounding (this can be done using mechanical force say small mortar or electrical force say ball mill)

2. Heating (this can be done using small or big heating furnaces)

**1. Grounding:** - While grounding the compounds one should be careful of any type of contamination for example sometimes the grinder particles may be added. Usually the grinders which were shown in the below figure are called mortars with a pestle which are made of with a material ‘agate’ which is not react with other particles while grinding. These are available in the market also.

![Mortars with a Pestle](image)

**Fig.3.1.1b Mortars with a Pestle**

**m. Crucibles and atmospheres:** -
n. Furnace for Heating the Specimens: - A muffle furnace of muffle sizes 25 X 25 X 25 cm is used for preparing the phosphors. The samples of synthesized phosphor were heated up to 1200°C for three hours in a furnace made by ‘Precision Control’. The furnace has a very precise temperature controller of ‘Eurotherm’ make, with a resolution of ±1°C. A mechanical protection system is provided so that the input current to the heating elements would be cut-off, once the temperature reaches 1200°C. However in the present investigation heating required is 1200°C. Other phosphor synthesis techniques are briefly discussed bellow.
The phosphors materials for any application can be synthesized by sol-gel process which includes oxides, sulfides, oxysulfides, halides, silicates, borates, phosphates, tungstates and molybdates can be synthesized by sol-gel process. The main advantages of sol-gel process are dispersions of colloidal particles in a liquid. The gravitational forces on the particles are negligible. Synthesis of nanophosphors by sol-gel process can be described in the following steps:

a) Reacting dilute solution comprising source of organic or inorganic metal salts, and an organic precursor providing source of boron, silicate, phosphate, sulfide, etc.

b) Refluxing the solution in required composition in an acid or alkaline medium to form a gel.

c) From a sol, a gel is formed with an interconnected, rigid network, having nanometer pores and a polymeric chain whose average length is of the order of sub-microns.

d) Converting gel into xerogel, aerogel by drying in air at low temperatures (40 to 60°C) for submicron or in vacuum for nano size particles or gel powder by spray drying and thermally decomposing the xerogel or aerogel powders at temperatures below solid state reaction temperatures. Particle size ranging from nano to submicron depends on calcinations temperature.

3.1.3 Spray Pyrolysis process:

In recent years, spray pyrolysis has become another method to prepare sub-micron and spherical shape phosphors. Here, an ultrasonic spray generator is used to generate fine droplets of suitable precursors to the phosphor to be prepared. Every phosphor particle is of high phase purity as each particle arises from one droplet in which constituents are mixed homogeneously. The preparative conditions, concentration of precursors, nature of additives and flow rate controls the size and morphology of phosphor particles. When the droplets are dried, decomposed and crystallized in dispersed phase when passing through a reactor at high temperature for a short time (seconds).

3.1.4 Combustion synthesis:

Combustion synthesis has been proposed to prepare oxide-based phosphors of smaller size particles. This method involves a highly exothermic reaction between an organic fuel and metal salts (oxidizers) in an aqueous solution. The reaction is initiated at low temperatures (around 500°C) and proceeds to
completion in a few minutes. The peak reaction temperature depends on the fuel and oxidizer molar ratio (f/o).

3.2. Characterization Techniques:
For any good analysis of the synthesized products good characterization is required to get an insight into the nature, type and characteristics of the product. The details of the experimental set up and the tools having been used for characterization of the synthesized phosphor have been elaborated in this chapter. The tools used for characterizations of prepared phosphor materials in this study are as follows:

(a) X-ray diffraction technique (XRD).
(b) Scanning Electron Microscopy (SEM).
(c) Spectrofluorophotometer (SPF).
(d) Thermoluminescence (TL) Glow curve recorder.
(e) Fourier Transform Infrared Spectroscopy (FTIR).
(f) Particle size analyzer.

3.2.1 Spectrofluorophotometre: -
The three principle components of this instrument are the source of excitation, the sample cell and the detector. The source is either mercury or a xenon arc. The mercury arc gives very high intensities at its emission lines. The advantage with the xenon arc is that the lines are uniformly distributed over the range of frequencies most commonly used, although the intensity is low compared to the mercury lines. The xenon lamps are used extensively. Going to the working of the instrument, the light from the source passes through the device used to select the excitation radiation, often being focused in order to obtain increased intensity. This device may either be a filter or a monochromator. Filters give a greater quantity of light but the selectivity is poor. Interference filter can provide much better selectivity. In case of monochromators, the one having a prism has the advantage of greater intensity in the ultraviolet region, which is usually needed for excitation. However quartz prism, which are needed for dispersion in this region are quite expensive. The light loss with monochromators is often less than that with a prism one but the problem of overlapping spectra due to the passage of different orders can be serious. Commercial instruments are found with either prism or grating monochromators, in general. The sample cell should be made
of material, which does not absorb appreciably the wavelength of interest. In most cases a good grade of glass is suitable however, for region below 250 nm, quartz cell should be used. A right angle arrangement is generally used for placing the cell with respect to the excitation and detection components.

The fluorescence leaving the sample cell usually passes directly into a filter, which is used to eliminate any scattered light of the excitation frequency, or into a monochromater is used. This monochromater, called fluorescence or emission monochromater is usually of grating type. Since it normally provide better dispersion and less light loss than a prism system. When using monochromators for both the excitation and emission components, the problem of slit width becomes particularly important. Even when using high intensity sources, the amount of excitation light hitting a sample is small, and the fluorescent light leaving the sample is even smaller. This small fluorescence is then passed through another monochromater, i.e. emission monochromator, before being detected.

![Fig. 3.2.1a Spectrofluorophotometre](image)

1. Xenon lamp, 150 W
2. Ellipsoidal mirror, SiO2-coated
3. Slit Assy., excitation side
4. Concave mirror
5. Concave grating (for excitation)
6. Beam splitter quartz plate
7. Teflon reflector plate I
8. Teflon reflector plate 2
9. Optical attenuator
10. Photomultiplier for monitoring, R212-14
11. Condenser lens (dual-lens)
12. Cell
13. Condenser lens
14. Slit Assy., emission side
15. Concave grating (for emission)
16. Concave mirror
17. Photomultiplier for photometry, R3788-02
18. Focal point
19. Inlet Slit
20. Outlet slit
21. Aperture for light quantity balancing

Fortunately, it is seldom necessary to have small slit width on both chromators simultaneously. When recording emission spectra the slit of excitation monochromater can be large and when recording excitation spectra the slit on the emission monochromater can be large. The instrument needs a highly sensitive detection system. In most instruments, high gain photomultiplier tubes with their requisite. High voltage power supplies are necessary. Some systems measure under DC condition, while others use a chopped light beam and incorporated tuned AC amplifiers. The DC system, although less complicated, are inconvenient for differentiating fluorescence and Phosphorescence. The output of the detection system can be displayed in several ways. Simply a meter an oscilloscope or a Recorder can be used. For particularly low level signals, where the signal to noise ratio is the limiting factor, integrator with large time constant circuits can be advantageous.

The excitation and emission spectra of the synthesized phosphors have been recorded on a 'Shimadzu' system. The Shimadzu Model RF-5301 PC is a high-resolution fluorescence spectrophotometer. The detector used is the Shimadzu make photomultiplier (type no R928 of multialkali photocathode), which has a flat spectral response over the entire range of wavelength of measurement i.e. from 220 to 900 nm.
For spectral measurements, the phosphor powder is loaded in metallic plaque having a quartz window and placed on the sample compartment using a solid sample holder. A collimated monochromatic beam of UV rays from the excitation monochromater falls on the phosphor surface at angle of $45^\circ$ and the luminescent light emitted enters through the entrance slit to the emission monochromator. From the emitted light, one of the prominent emission lines is selected by the emission monochromator and held fixed for signal detection by the PMT. The excitation monochromator is now continuously scanned from as low as 200 nm upward up to the lower limit of the emission region, until the recorder records spectrum. The instrument has an emission monochromator of high resolving power with a range upward of 900nm, which covers the entire visible range. From the previously recorded excitation spectrum, any wavelength of interest in the UV range can be selected for exciting the phosphor. The emitted light from the phosphor plaque window enters the entrance slit of the emission monochromater, which is being continuously scanned over the entire visible region of interest, and recorded.

Fig.3.2.1b Block diagram of a Spectrophotometer

1) Excitation monochromator
2) Cell holder
3) Emission monochromator
4) Monitor side photomultiplier tube
5) Fluorescence side photomultiplier tube
Several filters of the Corning series are provided to prevent the excitation wavelength and its higher orders from getting recorded erroneously as emission peaks. A 150 W xenon lamp is used as a source. Concave gratings of 900 lines per mm are used on both the excitation and emission sides for monochromater. Block diagram of a Spectrophotometer is given in Fig.2.2.

Software Specifications:
1. Operating principle: -
The light emitted from the xenon lamp enters the excitation port. The beam splitter splits the light emerging from the excitation port and is directed to the monitor detector. A shutter is provided between the excitation port and the sample, and it is placed into the optical path as commanded from the panel. All the driving components that is, wavelength drive motors, slit controls motors and control for the shutter are operated by signal sent from the computer. The output signal from the monitor detector and fluorescence detector (photomultiplier) are processed by the computer via A/D converter and transmitted to the CRT or graphic plotter individually determined. The model employ the most sophisticated data correction technique to ensure that we get accurate and reproducible fluorescence spectra. Since the measurements are affected by the response characteristic of the spectrometer and the optical components such as the gratings and detectors. To compensate for these responses, the radiometric correction factors for the system and applies via DM3000F software.

2. Measurement Procedure: -

A solid sample holder is provided with the fluorometer. It enables collection of front face fluorescence at an angle of 22.5°. The powder sample was spread on it. The sample holder was fixed into sample compartment. When analyzing the sample, optical axis runs along the centerline of powder surface.

First the excitation spectra were recorded by setting the emission wavelength at the zero order and keeping other parameters as specified in the manual. The excitation bands were identified from these spectra and the emission spectra were scanned for identified excitation wavelength. This was necessary to know the approximate nature of EX spectrum, so it is necessary to select a particular band in the emission for scanning the excitation. Therefore for proper excitation spectra the emission wavelength was set at the position as identified from the earlier emission spectrum. The excitation and emission spectra were recorded with spectrometer slit fixed at 1.5 mm.

3.2.2. Thermoluminescence (TL) Glow Curve Recorder: -

The thermoluminescence glow curve reader consists of a specimen holder along with heater plate and a temperature controller programmer, a photomultiplier tube as detector, a high voltage unit, a D.C. amplifier and a suitable displaying or recording device, as shown in Fig. 3.2.2a.
The specimen is spread uniformly (5mg weighed) over a metallic strip of Kanthal (Fe-72 %, Ce- 23 %, Al – 3 %, and Co – 2 %). The strip is narrow and has a circular depression of 15 mm at its center. A chromel-alumel thermocouple is spot welded to record the temperature of the specimen. A linear relationship between the rise in temperature and time is maintained by the uniform heating rate that is controlled by the temperature programmer. The photomultiplier tube is housed in a light-tight cylinder and a high voltage is applied to it. When the kanthal strip is loaded with the irradiated specimen, who is placed in front of the photomultiplier window, the light emitted by the specimen during heating is recorded through the photomultiplier window. The light emitted by the specimen during heating is detected by a photomultiplier tube and is recorded through D.C. amplifier by the output device.
In the present study, the thermoluminescence glow curves of the samples were taken on a Nucleonix make Windows Based thermoluminescence reader. The system consists of PMT housing with drawer assembly, high voltage module, D.C. amplifier module, Temperature controller unit, power supply unit, AD-DA card and a personal computer system along with required hardware and software. Block diagram is given in Fig 3.2.2b.

The following is the procedure for making the TL measurements.

**Radioactive Sources for Irradiation:**

The thermoluminescence of sample was studied after irradiation using a $\gamma$-rays as well as $\beta$-rays. For $\gamma$-irradiation, a Co$^{60}$ gamma ray source is used having a biological
shield, central drawer incorporating the sample chamber, driving system, control panel and external cabinet. The central drawer can be moved up and down as required and this movement is controlled by the front control panel, through an electrical circuit. In the present investigation 1Gy γ-irradiation (1000 rads) test dose is given to all synthesized samples. For β- irradiation Sr-90 source is used and test doses of 1Gy, 5 Gy as well as 20 Gy is given to study the dose effect on the phosphor. The TL reproducibility of phosphor is found to be ± 2 %.

**How to make TL measurements more accurate using Nucleonix PC based TL reader system:**

I. Precautions to be observed for measurements with TL materials in powder Form:

a. It is very important to measure the powder accurately and place it into the kanthal strip.

b. Accuracy depends mainly on the accurate weight measurement.

c. Powder should not be placed on the kanthal strip as a heap should be spread uniformly. This ensures that while heating takes place all the particles in the powder get heated up to the same temperature.

d. While disposing from the kanthal strip, it should be gently brushed aside, so those powder particles falls on to the collection tray.

e. Any particle left out may contribute to the next measurement as a residual TL adding to the next sample, measurement being inaccurate to that extent.

II Choosing appropriate heating profile

a. Depending on the type of TL material (CaSO4, LiF or other material) and the form in which it is used (disc, rod, chip, powder crystals, pellets etc.) the heating profile is to be chosen.

b. The purpose of choosing most appropriate heating profile is primarily to maximize TL output and leave minimum residual TL in it. Also to minimize the contributions due to thermal and IR emissions.

**3.2.3 X-Ray Diffractometer (XRD):**

**X-ray Diffraction:**

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X-ray diffraction is one of the most promising and extensively used tools for any material characterization today. A tool used as a fingerprint for determination of crystalline material and for determination of their crystal structure. All crystalline materials have atoms in a regular periodic arrangement which is lacking in amorphous materials. Atoms are arranged in a three dimensional frame of points created by translation vector defined in terms of three fundamental translation vectors a, b and c known as lattice. A lattice is a periodic arrangement of a smallest chosen block, called unit cell. The crystalline solid can be classified within the seven crystal systems, which are further sub divided into 14 Bravis lattices.

**Basic theory of (X-ray) diffraction:**

The periodic lattice found in crystalline structures may act as a diffraction grating for wave particles or electromagnetic radiation with wavelengths of a similar order of magnitude (10-10m / 1 Å).

For solids there are three particles/waves with wavelengths equivalent to interatomic distances and hence which will interact with a specimen as they pass through it:

**X-Rays, electrons and neutrons:**

In materials with a crystalline structure, X-rays scattered by ordered features will be scattered coherently “in-phase” in certain directions meeting the criteria for constructive interference → signal amplification.

The conditions required for constructive interference are determined by Braggs’ law.

Bragg’s Law, \(2d \sin \theta = n\lambda\).

- \(\lambda\) = X-ray wavelength
- \(d\) = distance between lattice planes
- \(\theta\) = angle of incidence with lattice plane
- \(n\) = integer.

**The X-ray diffraction experiment:**

When reduced to basic essentials, the X-ray diffraction experiment fig.3.2.3a, requires an X-ray source, the sample under investigation and detector to pick up the diffracted X-rays.

**The powder method-principles and uses:**
The principles of the powder method are shown in fig.3.2.3b. A monochromatic beam of X-rays strikes a finely powdered sample that, ideally, has crystals randomly arranged in every possible orientation. In such a powder sample, the various lattice planes are also present in every possible orientation. For each set of planes, therefore, at least some crystals must be oriented at the Bragg angle, θ, to the incident beam and thus, diffraction occurs for these crystals and planes. The diffracted beams may be detected either by surrounding the sample with a strip of photographic film (Debye-Scherrer and Guinier focusing methods) or by using a movable detector, such as a Geiger counter, connected to a chart recorder (diffractometer). The original powder method, the Debye-Scherrer method, is little used nowadays, but since it is simple it is instructive to consider its mode of operation. For any set of lattice planes, the diffracted radiation forms a surface of a cone, as shown in figure-5.29. The only requirement for diffraction is that the planes be at angle θ to the incident beam; no restriction is placed on the angular orientation of the planes about the axis of the incident beam. In the finely powdered sample, crystals are present at every possible angular position about the incident beam and the diffracted beams that result appear to be emitted from the samples as the cone of radiation. A powder pattern has three main features that may be measured quantitatively. In decreasing order of relative importance, these are (a) d-spacings, (b) intensities and (c) line profiles.

**Effect of crystal size on the powder pattern: Particle size measurement**

Phase identification: Each crystalline substance has its own characteristics powder diffraction pattern which may be used for the identification. Standard patterns are given in the Powder Diffraction File (known as the JCPDS File or, formerly, as ASTM Files). The inorganic section of the File now contains over 35000 entries and is increasing at the rate of about 2000 per year. The powder X-ray method may be used as a rough check on purity provided the impurities are present as a separate crystalline phase(S). The lower limit of detection of impurity phases in routine work is usually in the range of 1 to 5 percent.

X-ray powder diffraction may be used to measure the average crystal size in a powdered sample, provided the average diameter is less than about 2000Å. The lines in a powder diffraction pattern are of finite breadth but if the particles are very small...
the lines are broader than as usual. The broadening increases with decreasing particle size. In the absence of extra broadening due to small particle size, powder lines or peaks have a finite breadth for several reasons: the radiation is absolutely monochromatic, the Kα line has an intrinsic breadth due to Heisenberg’s uncertainty principle and the focusing geometry of the instrument may not be perfect for a variety of reasons. In order to understand why small particle size leads to broadening it is necessary to consider the conditions under which diffraction may occur if the incident angle is slightly different from the Bragg angle, θB. The commonly accepted formula for calculating particle size is the Scherrer formula:

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

Where d is the thickness of the crystal (in angstroms), \( \lambda \) the X-ray wavelength and \( \theta_B \) the Bragg angle and \( \beta \) is the Line Broadening (Full width Half-maximum in radians).

The main advantages and importance of X-ray diffraction are as follows:

(a) A powder pattern is a crystal’s ‘fingerprint’.
(b) Qualitative phase analysis can be efficiently done.
(c) The shape and size of the unit cell can be estimated.
(d) The atomic number and position of the various atoms in a cell.
(e) From the d-spacing of the X-ray diffraction pattern the crystallite size can be determined.
(f) Determination of the lattice parameters, like, a, b, c, α, β, γ and thus the crystal structure.

![Fig. 3.2.3a Bragg’s law.](image-url)
3.2.4 Scanning Electron Microscope (SEM): -

Electron microscopy is an extremely versatile technique capable of providing structural information over a wide range of magnification. At one extreme scanning electron microscopy (SEM) compliments optical microscopy for studying the texture, topography and surface feature of powders or solid pieces; features up to tens of micrometer in size can be seen and, because of depth of focus of SEM instruments, the resulting pictures have a definite three-dimensional quality. The scanning electron microscope is an instrument, which is used to observe the morphology of a sample at higher magnification, higher resolution and depth of the focus compared to an optical microscope. Herein, an accelerated beam of mono-energetic electrons is focused on to
the surface of the sample and is scanned over it on a small area. Several signals are generated and appropriate ones are collected depending on the mode of operation. The signal is amplified and made to form a synchronous image on a cathode ray tube, the contrast resulting from the morphological changes and variation of atomic number over the area probed. A camera is used to photograph the image or it may be digitized and processed on a computer. The characteristics X–ray emitted may be analyzed for their energy and intensity (EAX), the energy being the signature of the element emitting them and the intensity as to how much of it is present.

SEMs are patterned gives following information:

**Topography**
The surface features of an object or "how it looks", its texture; detectable features limited to a few nanometers.

**Morphology**
The shape, size and arrangement of the particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching; detectable features limited to a few nanometers

**Composition**
The elements and compounds the sample is composed of and their relative ratios, in areas ~ 1 micrometer in diameter

**Crystallographic Information**
The arrangement of atoms in the specimen and their degree of order; only useful on single-crystal particles >20 micrometers

**Requirement for SEM and typical operating parameters**
(1) Electrons, being charged particles, require vacuum environment for traversing without change in their number and density.

(2) The sample to be analyzed need to be electrically conducting, otherwise there is a charge buildup due to the impinging electrons which gives rise to jumping of the beam and hence its instability.

Thus the sample has to be vacuum compatible and electrically conducting.

Typical operating parameters are: Vacuum~ $10^{-6}$ Torr; Electron energy~ up to 50 KeV; depth probed ~ 100A to 1 μm, resolution~ 60 A and depth focus ~ 15 μm at 10000X.

X-radiation mode (EAX)
In this mode, one employs (i) large beam diameters up to 1 μm; (ii) large beam currents and (iii) long integration time for adequate signal to noise ratio. Sampling volume is rather large and the resolution limited. X-rays may be collected either in dispersive or non-dispersive mode. In the dispersion mode, one uses a spectrometer equipped with various analyzer crystal combinations (e.g. LiF/ADP; RAP/Lead Sterate) together with a proportional flow counter detector and each element is collected, one at a time, at a separate angle setting. On the other hand, in non-dispersive mode, a liquid nitrogen cooled Li drifted silicon or germanium detector along with a multi-channel analyzer, is made use of to detect all the elements simultaneously. Each of the methods is amenable to obtain images corresponding to the distribution of single element.

Sample preparation

Biological samples are specially treated to immobilize them and render them vacuum compatible without appreciable change in their surface morphology. Surface of nonconductive materials are rendered conductive usually by coating a thin (100A) metal film of aluminium / gold / gold-palladium / carbon, the last one being specifically suited for EDAX. The materials can also be observed at low primary energy, at which the coefficient for secondary emission is ~ 1 and charge buildup is negligible. Entire sample preparation consists of mounting the sample on a metallic platform via a conducting path.

Stability of the sample

Electron beam current has to be within suitable limits. Most of the incident power is dissipated in the form of heat, which may induce changes in the sample composition due to decomposition and / or diffusion. For a target of good thermal conductivity, the heating effect is negligible whereas poor conductivity samples may pose problems. A thin, grounded conducting layer, normally deposited, simultaneously serves as a charge bleeder and a heat sink. The layer will, however, decelerate the incident electron beam and may also attenuate the escaping x-ray radiation, thus posing an upper limit for the film thickness, which depends on the incident electron energy, the absorption edge energy and the mass absorption coefficient in the film material.
3.2.4 Fourier Transform Infrared Spectroscope (FTIR):

FTIR – Introduction

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitative some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments.

Qualitative Analysis

FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques.

Physical Principles

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E₀) and the first excited state (E)]. The energy corresponding to these transitions between molecular vibrational states is
generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

Sample Preparation

Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, and is frequently used for polymer identification.
3.2.6 CIE -1931 color space:
The measurement of colour and intensity of radiative transition and their relation with human eye susceptibility constitute an integral part of luminescence. An essential tool known as photometry is used to measure radiation of only visible region of the
electromagnetic spectrum. It forms a basis for determining the qualitative relationships existing between the physical concepts of radiation and the psycho-
physical concepts like ‘sensation’ caused in the observer’s eye by the radiation under the study. This type of approach becomes inevitable when properties related to emission colours, persistence etc. are to be studied thoroughly. The effectiveness of light radiation for stimulating the human eye is given by the relative eye sensitivity \( V(\lambda) \), which is a function of wavelength. Figure-11 indicates the relative eye sensitivity, as defined for a 2\(^\circ\)-viewing angle by the Commission Internationale de l’Eclairage (CIE) for normal photopic vision. The value of \( V(\lambda) \) is highest at 555nm and falls to nearly zero at the extreme ends of the visible spectrum at 390 and 770nm. The effectiveness of the available radiant energy on vision (luminosity) at wavelength 555nm is 680 lm W\(^{-1}\). In other words, for normal photopic (bright environment) vision at the peak sensitivity of eye (555nm), 1 W of radiant energy is equivalent to 680 lm. However, for a scotopic (dark environment) vision the eye sensitivity is high at 507nm and radiant energy is equivalent to 1700 lm W\(^{-1}\). Hence, development of long persistent phosphors emitting in this region gains utmost importance. The colours that can be treated and measured in terms of chromatic response of the eye to pure colours of different wavelengths are called psychophysical colours. These can be specified by using the coordinates of a chromaticity diagram, as shown in Figure-12. Although there are various systems to specify the coordinates, XYZ system is most accepted and adapted system. In the present study, the Equidistant-Wavelength method has been used to determine the coordinates on the colorimetric chromaticity diagram. The CIE coordinates for the samples have been calculated for CIE 1931, CIE 1960 and CIE 1976. Though the most common among them is the CIE 1931 but it suffers from drawbacks that are less with the CIE 1976, also known as uniform chromaticity scale diagram or the CIE 1976 UCS diagram commonly referred to as the \( u' \), \( v' \) diagram, which again is not free from errors but still has some better methodology to depict the graphs. A simple example would be of maps of the world, as it is not an easy job to represent a curved surface accurately on flat piece of paper, distortions occur. In some maps the countries near the one pole, such example Greenland, are represented too far compared to one near the equator like INDIA. On such maps, pairs of locations equally distant from one another on the earth’s surface are represented by points that are much closer together in India than in Greenland. No
map on a flat piece of paper can avoid this problem entirely, but some types of map are better than others in minimizing the effect.

**Uniform chromaticity diagrams**

Although the most common and most widely used notations in the field of colour representation are the chromaticity diagrams, but these suffer from serious disadvantage; the distribution of the colours on it is very non-uniform. Thus the representation of the same can be done by other ways, of them, the CIE 1976 uniform chromaticity scale diagram or the CIE 1976 UCS diagram, commonly referred to as the $u', v'$ diagram.

\[
u = \frac{4x}{-2x + 12y + 3}, \quad v = \frac{6y}{-2x + 12y + 3}
\]

\[
u' = \frac{4x}{-2x + 12y + 3}, \quad v' = \frac{9x}{-2x + 12y + 3}
\]

The values of the $u'$ and $v'$ for the spectral locus are given. The $u'$, $v'$ diagram was recommended by the CIE in 1976; prior to that a similar diagram, the $u$, $v$ diagram was used in which $u = u'$, and $v = (2/3) v'$. All chromaticity diagrams, whether $x$, $y$ or $u'$, $v'$ or $u$, $v$ have the property that additive mixtures of colours are represented by points lying on the straight line joining the points representing the constituent colours.

The position of the mixture point has to be calculated by the method given in section 3.5, and in the $u'$, $v'$ diagram the weights used are $m_1/v_1'$ and $m_2/v_2'$; and in the $u$, $v$ diagram the weights are $m_1/v_1$ and $m_2/v_2$. The $u'$, $v'$ diagram is useful for showing the relationships between colours whenever the interest lays in their discriminability.

CIE chromaticity diagram indicating division of color planes into areas corresponding to the individual color only for the CIE portion.
3.2.7 Particle size analyzer:

Introduction: Laser diffraction is the most widely used technique for particle size analysis. Instruments employing this technique are considered easy to use and
particularly attractive for their capability to analyze over a broad size range in a variety of dispersion media. The Mie solution is named after its developer, German physicist Gustav Mie. Mie theory, also called Lorenz–Mie theory or Lorenz–Mie–Debye theory is an analytical solution of Maxwell's equations for the scattering of electromagnetic radiation by spherical particles (Also called Mie scattering). For particles much larger or much smaller than the wavelength of the scattered light there are simple and excellent approximations that suffice to describe the behavior of the system. But for objects whose size is similar to the wavelength (e.g., water droplets in the atmosphere, latex particles in paint, droplets in emulsions including milk, and biological cells and cellular components) this more exact approach is necessary.

The formalism allows the calculation of the electric and magnetic fields inside and outside a spherical object and is generally used to calculate either how much light is scattered, the total optical cross section, or where it goes, the form factor. The notable features of these results are the Mie resonances, sizes that scatter particularly strongly or weakly. This is in contrast to Rayleigh scattering for small particles and Rayleigh-Gans-Debye scattering for large particles. The existence of resonances and other features of Mie scattering, make it a particularly useful formalism when using scattered light to measure particle size.

Mie Theory and the Fraunhofer Approximation:

When setting up laser diffraction methods, users are faced with the decision as to whether to use Mie Theory or the Fraunhofer Approximation to calculate the particle size distribution results.

The Fraunhofer Approximation represents the easiest model to set-up as, in contrast to Mie Theory, it does not require the user to provide any optical property information. However, its use can lead to significant errors due to the assumptions it makes regarding the nature of the materials being measured. As such, users need to consider the following when selecting the Fraunhofer Model:

**Particle Absorption**: If the particles show some transparency (absorption < 0.2), then the Fraunhofer approximation will tend to yield inaccurate results below 50µm in size. If the absorption is high (>0.2), good results may be obtained down to 2µm in size, although this does depend on the refractive index.
**Particle Refractive Index**: If the refractive index different between the particle and the medium which surrounds it is low, then the Fraunhofer model can shown errors, even up to very large particle sizes (>200µm).

**Particle Size**: If the particle size distribution contains material less than 2 microns in size then the Fraunhofer Approximation will lead to an incorrect assessment of the fine particle fraction.

The nature of the errors observed when using the Fraunhofer Approximation is not always predictable. In most instances an over-estimation of the fine particle fraction is observed, as shown here for a pharmaceutical material. However, it is also possible for the Fraunhofer model to underestimate the fine particle fraction, as is seen for materials such as calcium carbonate, because it incorrectly predicts the scattering efficiency of these particles.

In the present investigation the Mastersizer Micro system, Version 2.19 was used to find out the particle size shown in figure 3.9. The following are the technical details. Extensive market research and customer opinion directed the development of the Mastersizer Micro systems. The result is a small footprint, low cost instrument that takes laser diffraction out of the specialist laboratory and into the hands of particle technologists everywhere. The Micro is an instrument system in the clear Malvern tradition with no compromise on sample handling, Mastersizer Micro performs like a research machine and yet operates like a cost effective QC tool. The wide measuring range makes it ideal for application in fundamental studies and quality control of production lines in diverse industries such as pharmaceuticals, mining, minerals, clays, food, metal powders, emulsions, ceramics, polymers, pigments, paints and coatings to name a few. The Block diagram of the detection system is in figure 3.10.

**Easy Operation and Maintenance**: Single button operation means that inexperienced users can perform repetitive measurements easily and reproducibly. The stable single lens optics minimizes set up and routine maintenance.
Rapid data acquisition and analysis allows repeatable measurements to be made in less than 4 seconds. A unique "dip-in" probe provides sample agitation, sonication and circulation through the measuring system. By allowing the use of standard laboratory beakers as the sample tank, variable volumes of material can be analyzed.

**Superior Software – Complete Control:** Malvern software sets an acknowledged world-wide standard for instrument operation, data acquisition and handling, reporting and systems integration.

**Set up as easy as ABC:** A special "ABC" icon guides the user through a set-up routine ensuring that no parameters are over looked.

- **Mastersizer Micro’s Technical Specifications**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Mastersizer Micro: 0.3um – 300um</th>
<th>Mastersizer Micro-plus: 0.05um – 550um</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size Range</td>
<td>Mie scattering method</td>
<td>Mie scattering method</td>
</tr>
<tr>
<td>Measurement Principle</td>
<td>&lt; 4 seconds typical – user variable</td>
<td>He-Ne laser of wavelength 632.8nm</td>
</tr>
<tr>
<td>Measurement Time</td>
<td>± 2.0% on Dv50 on Malvern reference standard</td>
<td></td>
</tr>
<tr>
<td>Light Source</td>
<td>100-240V, 50/60Hz</td>
<td></td>
</tr>
<tr>
<td>Accuracy</td>
<td>500 (w) x 560 (h) x 325 (d) mm</td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>32Kg</td>
<td></td>
</tr>
</tbody>
</table>

Refractive index in the present study is taken as 1.5.

**Easy Mode:** a "GO" button runs the complete measurement to pre-selected requirements.

**Report Generation:** company logos, typestyles and formats can be incorporated into printouts.

**Flexible Data Processing:** a range of data processing options are available allowing the user to specify the graph format and scale.

**Statistical Analysis:** reproducibility of results and size trends can be reported using built-in statistical analysis options.

**Security Features:** four password access levels are available from supervisor down to a level for the infrequent or unskilled user.

Full Mie theory: full Mie theory matrix generator enables compliance with ISO13320. Advanced features: Malvern BASIC – a powerful set of programming tools enable the user to customize measurement parameters.
**Windows operation:** all the benefits of the Windows operating system are available to the Mastersizer user. A key feature is the ability to integrate particle size data by "cutting and pasting" into other independent software packages.

**Additional features for specific needs:** For measurement of solvent based systems, Malvern’s ospec small volume sample dispersion unit can be used, and when only very small amounts of material are available a direct injection small volume flow cell is available.

**Laser Diffraction:** Laser diffraction particle size analysis is based on the phenomenon that all particles scatter light at a range of angles, which is a characteristic of their size. Large particles scatter at small angles and vice versa. The Mastersizer Micro comprises a Helium-Neon laser as a light source, which illuminates the dispersed particles in the measuring zone. This is then focused by a Fourier lens to a detector, which consists of a large number of photosensitive elements radiating outward from the centre. A novel property of a Fourier lens is that it collects the scattered light from an ensemble of particles, and overlays the common angles of scattering on the detector array. The intensity of the scattered light is measured and using an optical model (Mie theory) to calculate the scattering pattern and a mathematical de-convolution procedure, a volumetric particle size distribution is calculated that best matches the measured pattern. The Mastersizer Micro produces volume-based measurements based on the measurement of ensembles of particles sampled at a rate of 500 snaps per second, simultaneously from all detectors. This means that the system is exceptionally suitable for the detection of rogue coarse particles.
Fig.3.2.7a Laser diffraction Particle size analyzer.

Fig.3.2.7b Block Diagram of the Detection System

References:
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