Chapter -3

Experimental Techniques

Spectrofluorophotometre, XRD, SEM
FTIR,Particle size analyser, CIE

This chapter describes the instruments: Spectroflurophotometer, XRD, SEM, FTIR, Laser diffraction particle size analyzer and the Commission International de l'Eclairage color co-ordinates used for the characterization of samples.

3.1 FURNACE

Thermal annealing treatment for the specimen was carried out in the muffle furnace. The muffle furnace with maximum 1200˚C heating capacity and control options was used for Thermal annealing treatment. The temperature was maintained with $\pm 1^{o}$C accuracy using a temperature controller. Alumina crucibles were used in the furnace and the heating rate of the furnace is 5^{o}C/min.

3.2 Spectrofluorophotometre

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.

i). Optical System of Spectrofluorophotometer:

The spectrofluorophotometer irradiates a sample with excitation light and measures the fluorescence emitted from the irradiated sample to perform a qualitative or quantitative analysis. A typical configuration of the spectrofluorophotometer [1-3] is schematically described, figure-3.1, taking the RF-5301 PC instrument as an example. The excitation monochromator (1) isolates a band of a particular wavelength from the light from the Xenon lamp to obtain excitation light. Since brighter excitation light will contribute to higher sensitivity of the spectrofluorophotometer, the excitation monochromator incorporates a diffraction grating with a larger aperture to collect the largest possible amount of light.The cell holder (2) holds a cell filled with sample. The emission monochromator (3) selectively receives fluorescence emitted from the sample and its photomultiplier tube measures the intensity of the fluorescence. This monochromator has a diffraction grating whose size is the same as that of the excitation monochromator to collect the greatest possible amount of light. The photomultiplier tube (4) is for monitoring. Generally, the Xenon lamps used on spectrofluorophotometers are characterized by very high emission intensity and an uninterrupted radiation spectrum. However, their tendency to unstable light emission will result in greater signal noise if

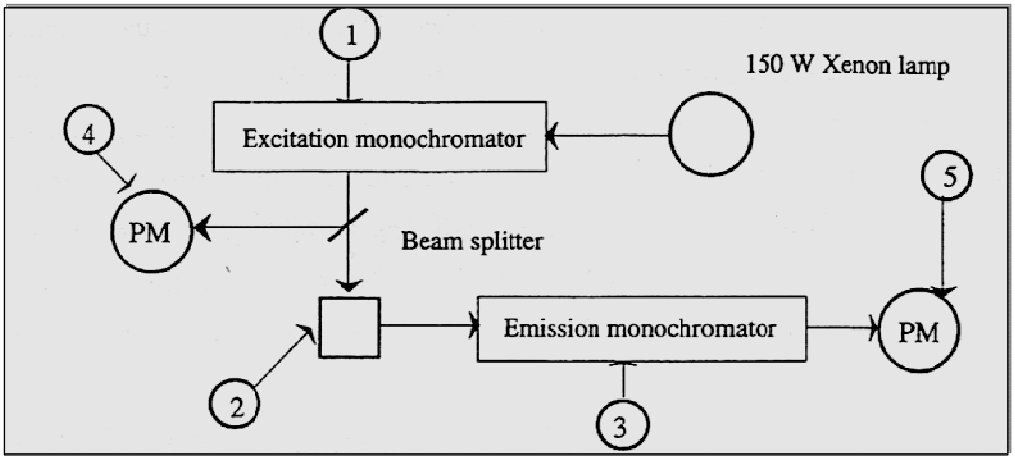
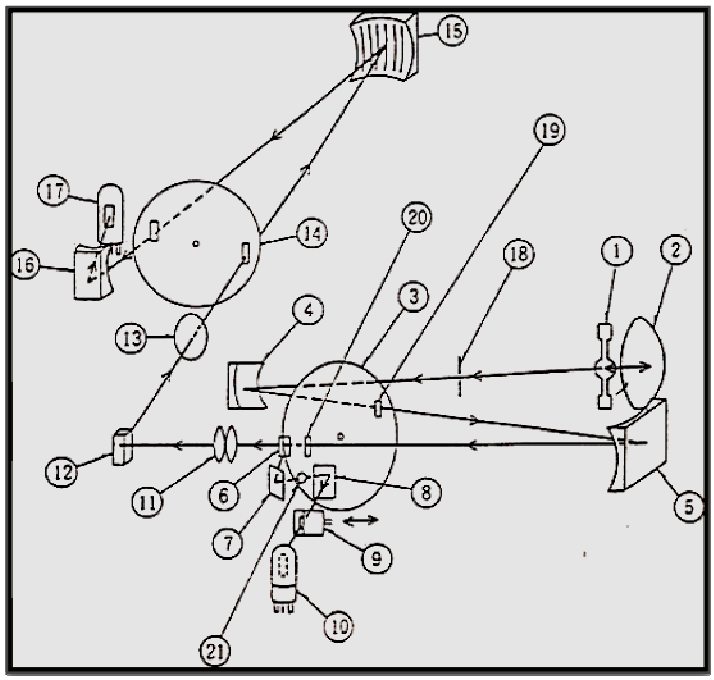


Figure.-3.1 Constitution of RF-5301 PC
(1) Excitation monochromator,(2) Cell holder, (3) Emission monochromator,
(4) Monitor side photo multiplier tube, (5) Fluorescence side photomultiplier tube



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

Figure-3.2 Optical System of RF-5301PC

no counter measure is incorporated. In addition, the non-uniformity in the radiation spectrum of the Xenon lamp and in the spectral sensitivity characteristics of the photomultiplier tube (these criteria are generally called instrument functions) causes distortion in the spectrum. To overcome these factors, the photomultiplier tube (4) monitors a portion of excitation light and feeds the resultant signal back to the photomultiplier tube (5) for fluorescence scanning.

ii). Design of the Spectrofluorophotometer

Figure-3.2 illustrated the optical system of the RF-5301PC instrument. A 150 W Xenon lamp (1) serves as the light source. The uniquely designed lamp housing contains generated ozone in it and decomposes the ozone by means of the heat produced by the5lamp. The bright spot on the Xenon lamp is magnified and converged by the ellipsoidal mirror (2) and then further converged on the inlet slit of the slit Assy. (excitation side) (3) by the concave mirror (4). A portion of the light isolated by the concave grating (5) passes through the outlet slit, travels through the condenser lens (11) and illuminates the sample cell. (The concave grating in both the monochromators is a highly-efficient ion-blazed holographic grating). To achieve light -source compensation, a portion of the excitation light is reflected by the beam splitter quartz plate (6) and directed to the Teflon reflector plate 1(7). The diffusely reflected light from the reflector plate I(7) then passes through the aperture for light quantity balancing (21) and illuminates the Teflon reflector plate 2(8). Reflected by the reflector plate 2 (8), the diffuse light is attenuated to a specific ratio by the optical attenuator (9) and then reaches the photomultiplier for monitoring(10). The fluorescence occurring on the cell is directed through the lens(13) to the emission monochromator that comprises the slit Assy. (14) and the concave grating (15). Then, the isolated lights introduced through the concave mirror (16) into the photomultiplier for photometry(17) and the resultant electrical signal is fed to the preamplifier.The spectra recorded using the above instrument displays the spectra along with the peak data the same can be copied to any other format, which is user-friendly software.

From routine analysis to research, employing highest level of sensitivity in the world compared to absorbance methods, fluorescence sensitivity is tens to thousands times better – this means that one can analyze nano grams to pico gram samples with great results. Fluorescence can be used also to identify a specific molecule in a complex background. When the compound of interest does not exhibit natural fluorescence, functional group-specific probes may be used to label the compound & assist our

research, the synchronous scanning mode allows mixtures of fluorochromes to be analyzes. The personal computer directly controls the instrument for data acquisition & processing. The windows friendly operating environment allows us to perform measurement, data processing, editing & recording in one continuous operation with a click of the mouse.

Using the copy graph function, measurement data or spectra may be easily transferred to word processing or spreads heat software for preparation of documents or additional calculations. The essence of fluorescence analysis is sensitivity; the high throughput optical system in the RF-5301PC employs a blazed holographic grating, photomultiplier monochromator slewing is conducted at an ultra-high speed of about & digital circuit to provide the highest level S/N ratio attainable. High speed scanning up to 5500 nm/min allows us to measure a spectrum in seconds. And since 20000nm/min, setting of two or more wavelengths can be performed quickly & easily. High resolution and extended range The band pass on the RF-5301PC may be set as narrow as 1.5nm, which makes is possible to distinguish fluorescent peaks from the background emission. The wave length range of 220 to 750 nm can be extended to 900nm with an optional R-928 photomultiplier. When the instrument is switched on, operating conditions of the spectrophotometer are automatically verified. Separately, a noise level (S/N ratio) & the light source (xenon lamp) usage are built in features to help maintain the instrument in its optimum condition, providing absolute confidence in either quality of the data. The sample compartment measuring 140mm, 170mm deep & 140mm high, enables use of micro cells, high sensitivity cells, or low cells, etc., for a wide range of applications. Unique high performance features in the RF-5301PC. Wavelength search functions allow the optimum excitation & emission wavelengths to be found in about two minutes. Vertical optics with dynode feedback, Vertical optics in the RF-5301PC minimizes light loss in measurement with an LC flow cell a micro cell or small test tube. This design assures exceptionally high signal to noise ratio and provides the ability to attain excellent analysis results using very small volumes of precious samples. The dynode feedback enhances RF-5301PC performance by raising or lowering negative high voltage to the detector in response to differences in the excitation energy at wavelengths. Dynode feedback which expands the dynamic range of the signal detecting system is significantly superior to ratio methods.

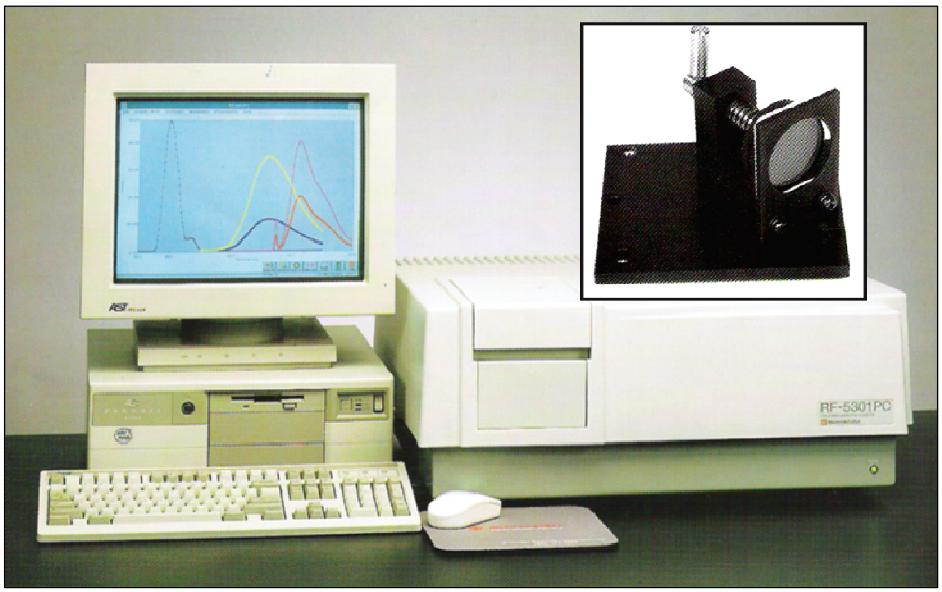


Figure-3.3 Spectrofluorophotometer- RF-5301 PC
with Powder Sample Holder

Table-3.1 Hardware specifications

Light source	150W xenon lamp. Ozone resolving type lamp housing
Excitation & emission mono chromators	Concave, blazed holographic grating,f/2.5, 1300 grooves/mm.
Wavelength scale	220-900nm
Measuring wavelength range	220-750nm & 0 orders as standard. 220-900nm with the optional R928 photomultiplier.
Spectral bandwidth	6-step selection of 1.5,3,5,10,15 & 20nm.(6nm bandwidth is available for half sample height on the excitation only)
Wavelength accuracy	±1.5nm
Light source compensation	Dynode feedback system with monochromatic light monitoring.
Sensitivity	The S/N ratio is 150 or higher for the Raman line of distilled water (350nm excitation wavelength, 5nm spectral band width, & 2 second response for 98% of the full scale).
Wavelength scanning	7-step selection of survey (about 5500nm/min), super (about 3000nm/min), very fast, fast, medium, slow & very slow.
Wavelength slewing speed	About 20000nm/min.
Response	8-step selection of 0.02, 0.03, 0.1, 0.25, 0.5, 2, 4& 8 seconds or 98% of the full scale.
Sensitivity selection	2-steps of high & low. (The sensitivity at high is about 50 times that of low).
Interface	RS-232C interface, interface for the auto sampler, and interface for sipper unit.
Dimensions & weight	667W*530D*270Hmm; 43 kg.
Power requirements	220V, 15 amps, 50Hz
Operational temperature range	
Operational humidity range	40-80 %(below 70% with temperature higher than 30 ^{o}C)

Table-3.2 Software Specifications

Measurement	Excitation, emission & synchronous spectrum measurement, time-course measurement, quantization, automatic search of optimal excitation & emission wavelengths, Popup Scan.
Data processing	Arithmetic calculation between spectra & between a spectrum & a constant, smoothing,1st through 4^{th} derivatives,1/Y,logarithmic conversion, data printout(with or without activity value computation),peak pick, point pick, area calculation, averaging(in quantization), generation of calibration curves of 1^{st} through 3^{rd} order.
Filing	Save, recall, & delete, of data. Conversion into ASCII & DIF formats.
Data output	Automatic scale adjustment, readout of data at user – specified point, data printout(preview function provided),selection of colors & types of curves
Maintenance	Automatic monitoring of signal-to-noise ratio, monitoring of the run time of light source lamp.
User interface	Speed –box (assigns icons for commonly used menu commands).
Other functions	Data exchange via clipboard, auto response control, and automatic shutter.
PC requirements	IBM-PC/AT or 100% compatible;! 486 or higher CPU; 8 Mbytes or larger main memory. Operates on MS – windows version 3.1 or higher.

Automatic shutter protects sample an automatic shutter in the RF-5301PC excitation path closes immediately when measurement ceases, thereby protecting the sample from photodecomposition. See the difference with windows performance working in the windows 3.1 environments makes operation intuitive. The software is driven by pull-down menus displayed at the top of your screen, which can be selected with just a click of the mouse. Many convenient and time saving features The RF-5301PC software is the ideal software to meet all our research needs, from teaching to method development and quality assurance. Follow changes in intensity over time for kinetic assays or perform quantitative analysis on several samples. One can save time & effort with features that allow for onscreen data manipulation.

Spectrum measurement mode Perform emission & excitation scans with ease, or overlay the two for interpretation. Obtain & differentiate excitation & emission spectra using color & line Pattern assignments. Zoom in using the mouse or zoom out with the radar function to auto scale all data on-screen. The software picks & tabulates peaks & valleys automatically and if one needs a fast spectral scan in any measurement mode, the pop up scan function displays it on- screen in seconds. Hardware specifications and Software Specifications presented in Tables-3.1 and 3.2. This is a simple but powerful for extensive data processing. Operations such as first through fourth order derivative, mathematical smoothing functions, log conversions & offsets are easily performed with the RF-5301PC software. Display up to ten spectral curves simultaneously or use mathematical transformations to maximize our results. Select the source & destination channels along with the desired calculation & the results are redisplayed on the screen.

iii). Measurement Procedure:

Figure-3.3 is the photograph of the 5301R PC along with solid sample holder. It enables collection of front face fluorescence at an angle of 22.5^{o}. 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.

3.3 POWDER X-RAY DIFFRACTOMETER

X-ray diffraction (XRD) is a versatile, non-destructive technique used to determine the crystallographic structure of natural and manufactured materials. It is also used in applications such as phase identification, grain size determination, composition of solid solution, lattice constants, and degree of crystalline in a mixture of amorphous and crystalline substances. A diffraction pattern is produced when a material is irradiated with a collimated beam of x-rays. The x-ray spectra generated by this technique provide a structural fingerprint of the material. The relative peak height is generally proportional to the number of grains in a preferred orientation and the peak positions should be reproducible. The X-ray diffractometer used in this study was an angle dispersive X-ray diffraction (ADXRD) beam line.

Basics of X-ray Diffraction:

About 95% of all solid materials can be described as crystalline. When X-rays are incident on a crystalline substance (Phase), one gets a diffraction pattern. In 1919 A.W. Hull gave a paper titled, “A New Method of Chemical Analysis”. Here he pointed out that “….every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others”.

The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases [4, 5]. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample.

Theoretical Considerations

The atoms are arranged in a regular pattern, and there is a smallest volume element that by repetition in three dimensions describes the crystal. This smallest volume element is called a unit cell. The dimension of the unit cell is described by three axes a, b, c and the angles between them alpha, beta, and gamma. An electron in an alternating electromagnetic field will oscillate with the same frequency as the field.

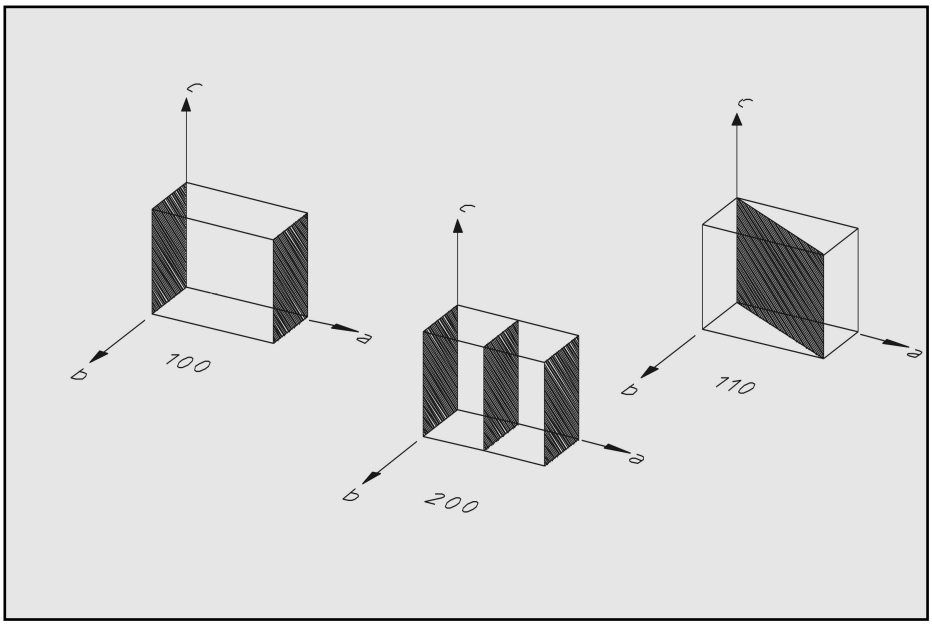


Figure-3.4 Orientation and interplanar spacing's of planes

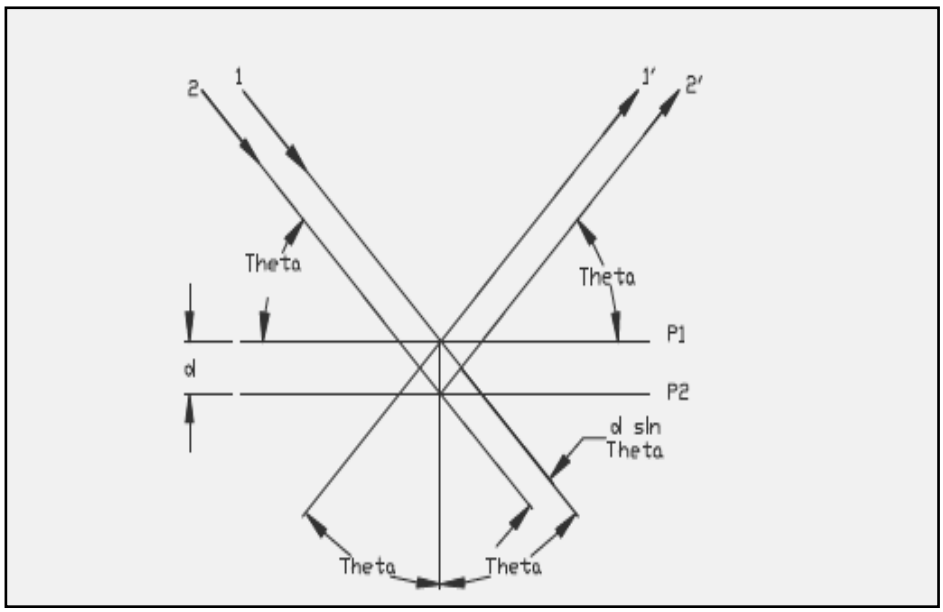


Figure- 3.5 X Ray's diffraction

When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions have destructive interference in almost all directions have destructive interference and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions have constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another.

This model is complex to handle mathematically. The orientation and interplanar spacing's of these planes are defined by the three integers h, k, l called indices. A given set of planes with indices h, k, and l cut the a-axis of the unit cell in h sections, the b-axis in k sections and the c- axis in l sections. A zero indicates that the planes are parallel to the corresponding axis. Figure-3.4 shows planes cut the- axis and the b– axis in half, but are parallel to the c- axis. If dimensional diffraction grating as a mathematical model, the three indices h, k, l become the order of diffraction along the unit cell axes a, b and c respectively. It should now be clear that, depending on what mathematical model we have in mind, we use the terms X-ray reflection and X-ray diffraction as synonyms. Let us consider an X-ray beam incident on a pair of parallel planes P_1 and P_2, separated by an interplanar spacing d, shown in figure-3.5.

The two parallel incident rays 1 and 2 make an angle θ with these planes. A reflected beam of maximum intensity will result if the waves represented by 1' and 2' are in phase. The difference in path length between 1 to 1' and 2 to 2' must then be an integral number of wavelengths, λ. We can express this relationship mathematically in Bragg's law, $2d \sin \theta = n \lambda$ [6-8].

The process of reflection is described here in terms of incident and reflected (or diffracted) rays, each making an angle θ with a fixed crystal plane. Reflections occur from planes set at angle θ with respect to the incident beam and generates a reflected beam at an angle 2θ from the incident beam.

The possible d-spacing defined by the indices h, k, l are determined by the shape of the unit cell. Rewriting Bragg's law we get: $\text{Sin } \theta = \lambda / 2d$.

Therefore the possible 2θ values where we can have reflections are determined by the unit cell dimensions. However, the intensities of the reflections are determined by the distribution of the electrons in the unit cell. The highest electron density is found around atoms. Therefore, the intensities depend on what kind of atoms we have and where in the unit cell they are located. Planes going through areas with high electron density will reflect strongly, planes with low electron density will give weak intensities [9, 10].

3.3.1Angle Dispersive X-ray Diffraction (ADXRD) Beam line

X-ray diffraction (XRD) is a powerful technique for studying the structure of materials - both crystalline as well as amorphous. The combination of high brightness and fine vertical collimation of synchrotron X-radiation with the added advantage of broad range of wavelength tunability as compared to conventional laboratory x-ray sources makes it an ideal source for XRD characterization of materials.

An angle dispersive X-ray diffraction (ADXRD) beam line has been setup and installed on BL-12 bending magnet port of the Indus-2 synchrotron. The electron source size at this port is approximately 0.5 mm (H) × 0.5 mm (V). The beam acceptance of the beam line is 2mrad (H) x 0.2mrad (V). The first optical element is a platinum coated pre-mirror (M1) which is plane and bendable and is used for vertical focusing/collimation of the x-ray beam. Double Crystal Monochromator (DCM) with Si (311) crystals is the second optical element of the beam line and is used for monochromatization of photon beam. Second crystal of the DCM is also used for the sagittal focusing of the beam. The third optical element is a platinum coated bendable post mirror (M2) used for vertical focusing/collimation of the beam. Depending upon the requirements of the planned experiment, the beam line can be operated in high flux, moderate energy resolution or moderate flux, high-energy resolution modes and high angular resolution mode. Figure-3.6 shows the optical layout of angle dispersive X-ray diffraction and figure-3.7 shows the photograph of the beam line.

3.3.2 Different modes of operation of beam line

Mode A (Focus mode)

The High flux moderate energy resolution mode is without post mirror. This mode of operation gives high flux but poorer energy as well as angular resolution·

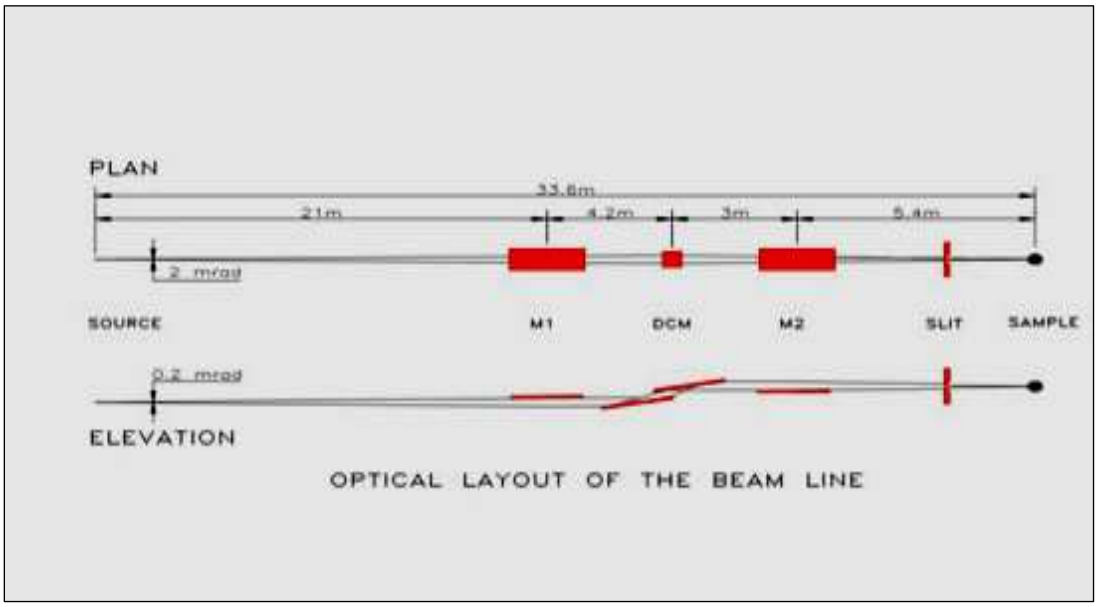


Figure-3.6 Optical layout

Figure-3.7 Photograph of the beam line

Mode B (Collimated mode)

This mode of operation gives high angular resolution-mode, in which the post mirror is kept unbent. Slits are placed to trim the beam to desired beam size.

Mode C

The High flux high energy resolution mode is with post mirror. This mode of operation gives high flux and high-energy resolution, but poorer angular resolution.

Photon beam Parameters

- Spectral Range: 5-20keV
- Spectral Resolution: 1eV at 10keV
- Flux: 10^{10} photons/sec at 10keV
- Beam Size:1mm (H) x 0.5mm (V)
- Angular Resolution:60”

3.3.3 Experimental Station

There are two experimental stations in tandem. The adaptive focusing optics allows us to focus the photon beam on one or the other experimental station. The first experimental station consists of a six circle diffractometer (Huber-5020) with Na I scintillation detector. The four circles consist of θ, 2θ, φ and χ rotations. φ and χ rotations are used to adjust single crystal samples. The second experimental station consists of an area detector (Image Plate Mar-345) for fast recording of XRD data on powder sample.

3.4 FOURIER TRANSFORM INFRARED SPECTROMETER

Fourier transform spectroscopy is a measurement technique where by spectra are collected based on measurements of the coherence of a radiative source, using time-domain or space-domain measurements of the electromagnetic radiation or other type of radiation[8]. It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (FTIR, FT-NIRS), and nuclear magnetic resonance.

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. Thus, the presence of specific functional groups can be monitored. The pellet samples for Fourier Transform Infrared Spectrometer (FTIR) measurements prepared based on 100mg: 2mg sample to KBr ratio. The produced samples were studied by IR Affinity-1 spectrometer and the wave numbers were set between 400 and 4000$cm^{-1.}$

Infrared Spectroscopy: Infrared spectroscopy has been a workhorse technique for material analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position)

Figure-3.8 IR Affinity-1

which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis [11-14].

IR Affinity-1

The IRAffinity-1 is a compact Fourier transform infrared spectrophotometer that is housed within an elegant form shown in figure-3.8. The interferometer is continuously optimized by a dynamic alignment mechanism, and a built-in auto dryer helps ensure ease of maintenance. The IRAffinity-1 offers the highest S/N ratio in its class (30,000:1, 1-minute accumulation, neighbourhood of 2,100 cm-1, peak-to-peak), a maximum resolution of 0.5 cm-1, and compact dimensions. Furthermore, the high-performance IR solution software, which emphasizes operability, and analysis support programs (Contaminant analysis program and Pharma Report program) make it easier to perform data processing and analysis.

The state of interference in an FTIR instrument is extremely delicate, and the interferometer must be controlled with high precision. With the IRAffinity-1, the moving mirror is run very smoothly and precisely by a flexible joint system, and the interferometer is optimized and stabilized by an improved dynamic alignment mechanism. This makes it possible to perform measurement in a stable state with a short warming-up time.

The state of interference of the He-Ne laser used for sampling by the interferometer is continuously monitored and compared with the state under the optimum conditions previously recorded by the system. The difference between these states is calculated by an advanced digital signal processor, and the inclination of the fixed mirror is changed continuously in order to eliminate any difference. This feedback is even provided during the sample measurement. There is also an automatic adjustment for the interferometer that performs this operation.

3.5 LASER DIFFRACTION PARTICLE SIZE ANALYSER

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 [15, 16].

3.5.1 Using 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.

Figure-3.9 Laser diffraction particle size analyser

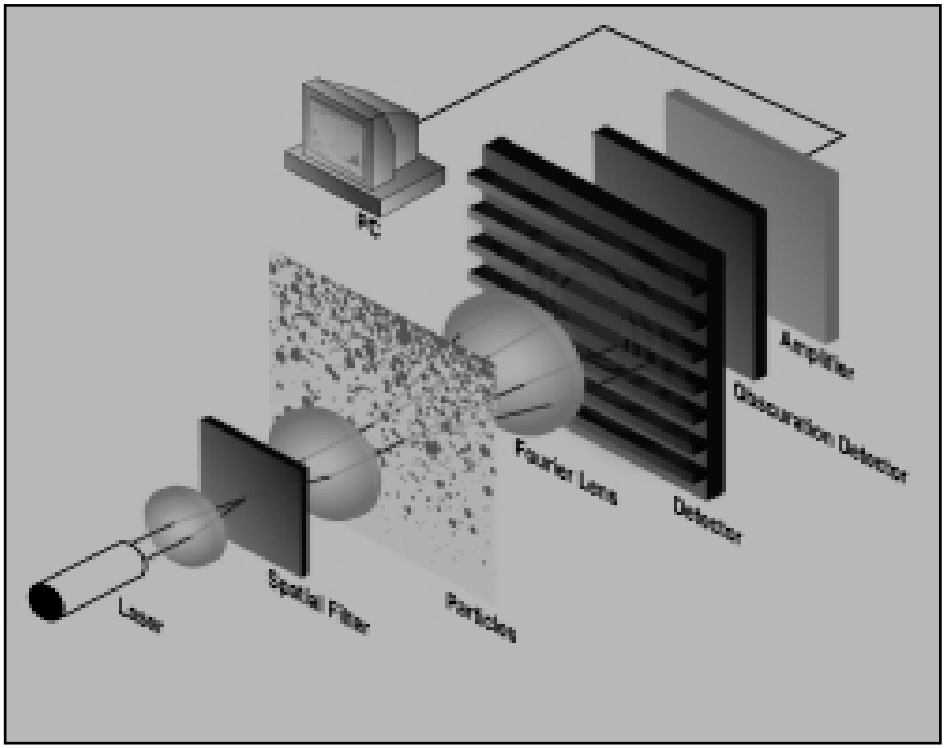


Figure-3.10 Block Diagram of the Detection System

3.5.2 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.

3.5.3 Mastersizer Micro's Technical Specifications

Size Range	: Mastersizer Micro: 0.3um – 300um
	Mastersizer Micro-plus: 0.05um – 550um
Measurement Principle	: Mie scattering me
Measurement Time	: < 4 seconds typical – user variable
Light Source	: He-Ne laser of wavelength 632.8nm
Accuracy	: ± 2.0% on Dv50 on Malvern reference standard
Power	: 100-240V, 50/60Hz
External Dimensions	: 500 (w) x 560 (h) x 325 (d) mm
Weight	: 32Kg

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 QSpec 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 deconvolution 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.

3.6 SCANNING ELECTRON MICROSCOPIC (SEM)

Scanning electron microscopy (SEM) is a technique in which a beam of energetically well-defined and highly focused electrons is scanned across a material (sample). The technique can provide material's information about topography and morphology. If the

system is equipped with energy dispersive X-ray spectrometer (EDS), it can also provide information about chemical composition of the material. The basic principle of the system is that, the electron beam impinges the surface and generates a splash of electrons with kinetic energies much lower than the primary incident electrons called secondary electrons.

The first SEM image was obtained by Max Knoll, who in 1935 obtained an image of silicon steel showing electron channeling contrast. Further pioneering work on the physical principles of the SEM and beam specimen interactions was performed by Manfred von Ardenne in 1937, which produced a British patent but never made a practical instrument. The SEM was further developed by Professor Sir Charles Oatley and his postgraduate student Gary Stewart and was first marketed in 1965 by the Cambridge Scientific Instrument Company as the "Stereo scan". The first instrument was delivered to DuPont.

An image of the sample surface is constructed by measuring secondary electron intensity as a function of the primary beam position. The SEM has many advantages over traditional light microscopes. It has large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, such that closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the user has much more control in the degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today [17-20].

The SEM images of powder phosphors in this study were obtained using Shimadzu super scan Scanning Electron Microscope model Philips XL 30 shown in Figure 3.11.

Philips XL 30 CP SEM

The Philips XL 30 CP is a conventional SEM with mouse-driven operation in a Windows environment. This system provides both secondary electron and backscattered electron imaging, along with an integrated EDAX system. The XL 30 offers a 4 axis motorized stage with full manual override. This is an excellent tool for both experienced and first-time users.

Figure-3.11 SEM Philips XL30

Philips XL30 is a new-generation, fully computer-controlled SEM. The fine electron source of the Lanthanum hexaboride single crystal system enables the attainment of much higher brightness source with a higher resolution images than a conventional tungsten filament SEM. Useful magnifications in excess of 200,000 times are obtainable, which translate to a resolution of 3.5 nm at an accelerating voltage of 30 kV.

Philips XL30 is a conventional SEM with optimum performance for both imaging and microanalysis of conductive and/or coated specimens. This makes the system ideal for research in many fields. With user friendliness a special benefit of the XL30, the instrument is an excellent tool for both the experienced and first-time user. The electron optical column with its conical final lens and fixed final lens aperture is optimized for high resolution imaging, X-ray microanalysis and low magnification performance. The fixed final lens aperture, column design and the computer controlled alignment guarantee alignment free selection of kV and spot size, even up to high beam currents. The integration of advanced electron optics and extensive system automation with a unique, high-level user shell has produced a precision instrument with exceptional levels of performance, flexibility and usability. In addition, an embedded EDX system can offer the user a total analytical capability within one single instrument. A mouse-driven instrument operating within MS-Windows NT environment, the XL30 is geared towards the future with direct communication networking, digital images for storage and remote printing.

The Philips XL30 is thus a multi-function, multi-user Scanning Electron Microscope. Not only is it capable of giving Secondary Electron images to 3.5nm resolution, but with its LaB6 filament is able to provide high quality Back-Scattered Electron images as well. This microscope is also equipped with a quantitative Energy Dispersive Spectrometer capable of chemical analysis with a detectable element range from B-U. A qualitative X-ray Mapping facility is also available. A cathodoluminesence detector is also supplied for looking at optical properties of materials. An Electron Back-Scattered Diffraction Pattern (EBSD) Camera is available which is able to determine sample orientation together with a Mapping Facility is able to provide sample details such as sample normal, coincident lattice sites, grain boundary disorientation, sample normal, pole figures, and diffraction pattern maps.

The XL30 SEM possesses modest frame store and image enhancement hardware and allows automated stage control, image capture, and image transfer between its computer and the centre's LAN network. Images can be saved to an industry standard TIFF file format for use in a variety of other programs for off-line image enhancement and manipulation. The sample stage can handle specimens up to 25 mm in diameter making it ideal for inspection of items such as metallographic samples.

3.7. CIE -1931 COLOR SPACE

The International Commission on Illumination (usually abbreviated CIE for its French name, Commission international de l'éclairage) is the international authority on light, illumination, color, and color spaces. It was established in 1913 as a successor to the Commission International de Photometric and is today based in Vienna, Austria.

In the study of color perception, one of the first mathematically defined color spaces is the CIE 1931 XYZ color space, created by the International Commission on Illumination (CIE) in 1931.

The human eye has receptors for short (S), middle (M), and long (L) wavelengths, also known as blue, green, and red receptors. That means that one, in principle, needs three parameters to describe a colour sensation. A specific method for associating three numbers (or tristimulus values) with each colour is called a colour space, of which the CIE XYZ colour space is one of many such spaces. However, the CIE XYZ colour space is special, because it is based on direct measurements of the human eye, and serves as the basis from which many other colour spaces are defined [21-23].

The CIE XYZ color space was derived from a series of experiments done in the late 1920s by W. David Wright and John Guild. Their experimental results were combined into the specification of the CIE RGB color space, from which the CIE XYZ color space was derived.

In the CIE XYZ colour space, the tristimulus values are not the S, M, and L stimuli of the human eye, but rather a set of tristimulus values called X, Y, and Z, which are also roughly red, green and blue, respectively. Two light sources may be made up of different mixtures of various colours, and yet have the same colour (metamerism). If

two light sources have the same apparent colour, then they will have the same tristimulus values, no matter what different mixtures of light were used to produce them.

The CIE x, y chromaticity diagram

Since the human eye has three types of colour sensor that respond to different ranges of wavelengths, a full plot of all visible colours is a three-dimensional figure. However, the concept of colour can be divided into two parts: brightness and chromaticity. For example, the colour white is a bright colour, while the colour grey is considered to be a less bright.The outer curved portion is the spectral (or monochromatic) locus, with wavelengths shown in nanometres version of that same white. In other words, the chromaticity of white and grey are the same while their brightness differs.

CIE 1931 Colour matching functions for 2° observer shown in figure-3.12.The three CIE colour matching functions (CMFs) are called X, Y and Z, and for practical color matching and display applications these can be treated as if they were the spectral response curves for the cone-receptors in the human eye.

A "colour" is defined by the *relative* stimulus of the eye's XYZ channels (the actual magnitudes will define the brightness or intensity). It makes sense therefore to define a colour by a *xyz* triplet which is normalised versions of *XYZ*:

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Z}{X+Y+Z}$$

Of course, by definition now, $x + y + z = 1$. As such, only two out of the three *xyz* coordinates are needed to uniquely define a colour. It is conventional to define colours by their *x*,*y* coordinates. This then gives rise to the CIE chromaticity diagram.

The figure-3.13 shows the related chromaticity diagram. The outer curved boundary is the spectral locus, with wavelengths shown in nanometres. Note that the chromaticity diagram is a tool to specify how the human eye will experience light with a given spectrum.

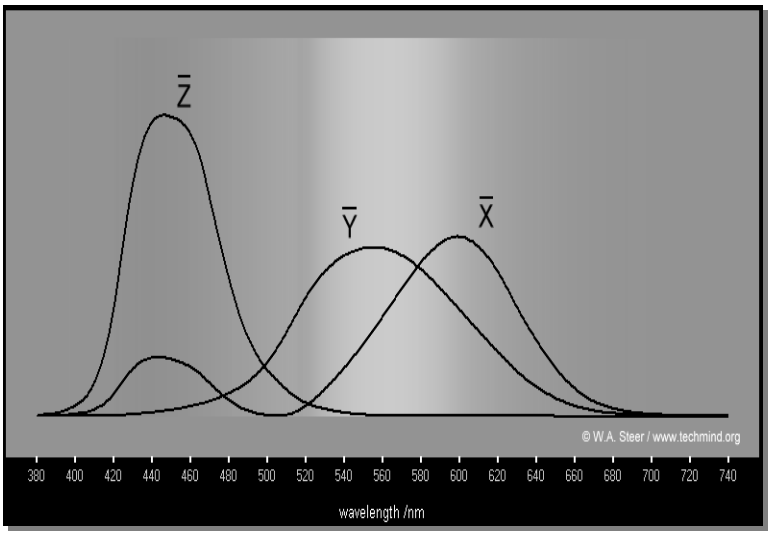


Figure-3.12 CIE 1931 Colour matching functions for 2° observer

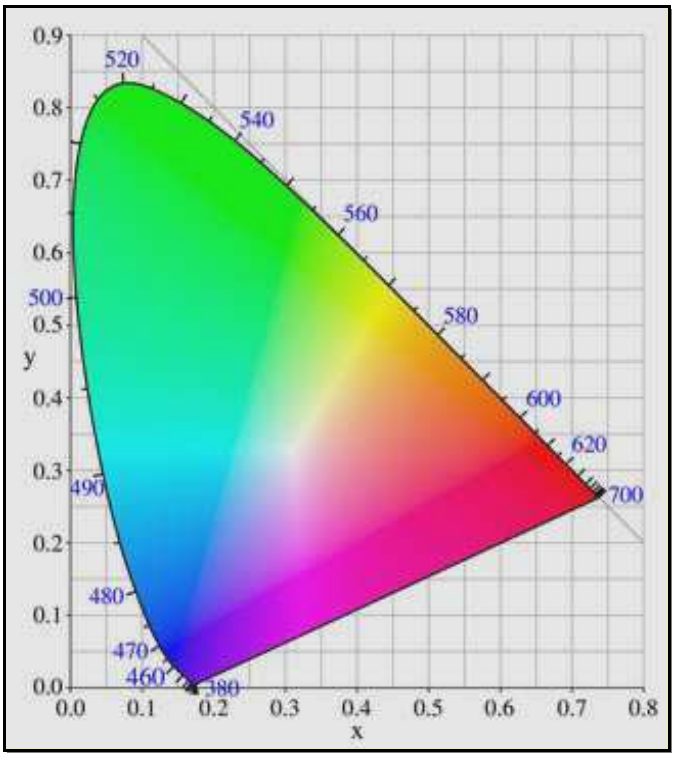


Figure-3.13 The CIE 1931 colour space chromaticity diagram

It cannot specify colours of objects (or printing inks), since the chromaticity observed while looking at an object depends on the light source as well.

Mathematically, *x* and *y* are projective coordinates and the colours of the chromaticity diagram occupy a region of the real projective plane.

- The chromaticity diagram illustrates a number of interesting properties of the CIE XYZ color space:
- The diagram represents all of the chromaticities visible to the average person. These are shown in color and this region is called the gamut of human vision.
- The gamut of all visible chromaticities on the CIE plot is the tongue-shaped or horseshoe-shaped figure shown in color. The curved edge of the gamut is called the spectral locus and corresponds to monochromatic light, with wavelengths listed in nanometers. The straight edge on the lower part of the gamut is called the purple line. These colors, although they are on the border of the gamut, have no counterpart in monochromatic light. Less saturated colors appear in the interior of the figure with white at the center.
- It is seen that all visible chromaticities correspond to positive values of x and y (and therefore to positive values of X, Y, and Z).
- If one chooses any two points on the chromaticity diagram, then all colors that can be formed by mixing these two colors lie between those two points, on a straight line connecting them. It follows that the gamut of colors must be convex in shape. All colors that can be formed by mixing three sources are found inside the triangle formed by the source points on the chromaticity diagram (and so on for multiple sources).
- The mixture of two equally bright colors will not generally lie on the midpoint of that line segment. In more general terms, a distance on the xy chromaticity diagram does not correspond to the degree of difference between two colors. Other color spaces (CIELuv and CIELab in particular) have been designed to meet this problem.
- It can be seen that, given three real sources, these sources cannot cover the gamut of human vision.
- Geometrically stated, there are no three points lying within the gamut that include the entire gamut.
- Light with a flat energy spectrum corresponds to the point (x,y) = (1/3,1/3).

REFERENCES

[1].Dieter.K.Schroder, Semiconductor Material and Device Characterization, Wiley, New York,(1990)

[2].Valdes, L.B., Proc. IRE 42, 420,(1954)

[3].Shimadzu RF 5301 PC Manual,(2003).

[4].Basics of X-ray Diffraction, chapter-7, Scintag Inc. Cupertino, CA,U.S.A,(1999).

[5].Ahmad Monshi, Mohammad Reza Foroughi, Mohammad Reza Monshi, World Journal of Nano Science and Engineering, 2, 154-160,(2012)

[6].Cullity, B.P.,Elements of X-ray diffraction,Addison–Wesley Inc.,(1978).

[7].Bish,D.L., Post, J.E., editors., Modern Powder Diffraction. Reviews in Mienralogy,20. Mineralogical Society of America(1989).

[8].Wall,B.,Driscoll,C., Strong,J., Fisher,E.: Physical Medical biology,1023-1034, (1982)

[9].Klug,H.P.,Alexander,L.E.,X-ray diffraction procedures for polycrystalline and amorphous materials. 2nd ed. Wiley, New York,(1974).

[10].Moore,D.M.,Reynolds,R.C.,Jr. X-Ray diffraction and the identification and analysis of clay minerals. 2nd Ed. Oxford University Press, New York, (1997).

[11].John Coates, Interpretation of Infrared Spectra:A Practical Approach, Encyclopedia of Analytical Chemistry,R.A. Meyers (Ed.),10815–10837,John Wiley & Sons Ltd, Chichester,(2000)

[12].Capron,M.,Douy,A., J.Am.Ceram.Soc.,85,12,3036-40,(2002).

[13].Katsumata, T., Sasajima, K.,Nabae, T.,J.Am.Ceram.Soc.81,413,(1998).

[14].Douglas.A.Skoog., F.James Holler., Timothy.A.Nieman., Principle of instrumental analysis, Harcourt Asia Pte, Ltd; Fifth edition, (1998)

[15].Rod,M.Jones,Particle size analysis by laser diffraction:, standard operating procedures,and Mie theory, Reprinted from American Laboratory,(2003)

[16].Stefánsson.A, Gunnarsson.I,Giroud.N, Anal.Chim.Acta,582,(2007).

[17].West,G.A.,Beeson,K.W.J. Mater. Res.,5,1573,(1990).

[18].Yen,W.M.,Shionoya,S.,Yamamoto,H.,Phosphor Handbook*(*CRCPress, Boca Raton, FL,(2006)

[19].Shinde,K.N.,Dhoble,S.J.,Adv.Mat.Lett.,1(3),254-258,(2010).

[20].Stringfellow,G.B.,Craford,M.G., Semiconductor and Semimetals, Academic Press, San Diego,48,(1997).

[21].Wright, William David., Colorimetry, Wiley Interscience. 9–24,(1981).
[22].John Guild, Philos. Trans. Roy. Soc. London, Ser. A 230, 149–187 (1931).
[23].Brand Fortner, Number by Color, Part 5,SciTech Journal 6, 32,(1996).