

MSc. Electronics 1st Sem.

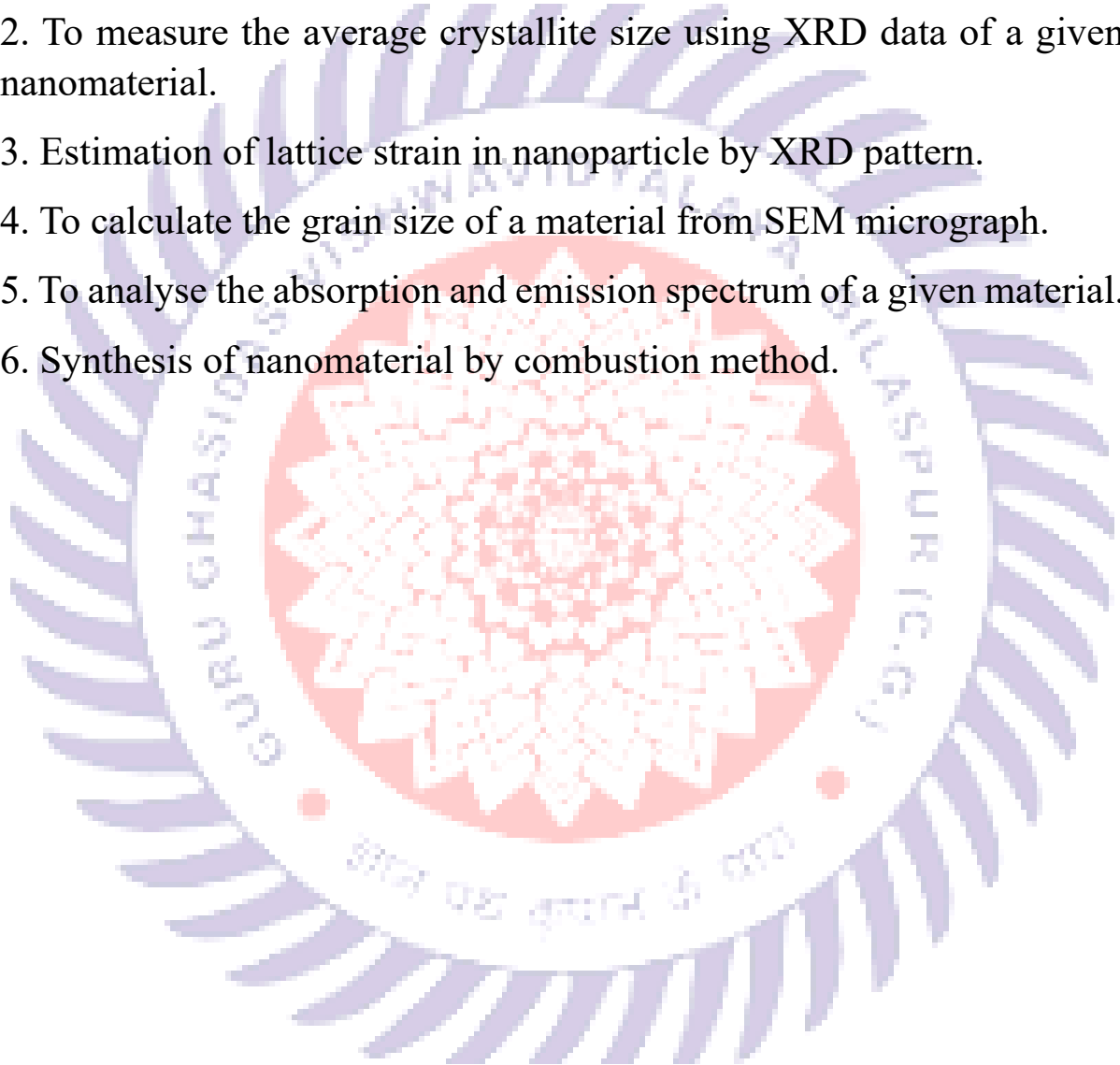
**Open Elective:
Applications of
Nanotechnology in
Electronics**

**Lab Course Code:
OPNPEL1**

Credits = 2 (0+0+2)

List of experiments

1. To calculate the energy bandgap of nanoparticle from UV-VIS spectra.
2. To measure the average crystallite size using XRD data of a given nanomaterial.
3. Estimation of lattice strain in nanoparticle by XRD pattern.
4. To calculate the grain size of a material from SEM micrograph.
5. To analyse the absorption and emission spectrum of a given material.
6. Synthesis of nanomaterial by combustion method.



Experiment No 1

Aim: To calculate the energy bandgap of nanoparticle from UV-VIS spectra.

Requirements: UV- Vis data of a sample.

Theory: Ultraviolet- visible (UV-Vis) spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference (or blank) sample. The band gap energy of a semiconductor describes the energy needed to excite an electron from the valence band to the conduction band. In 1966 Tauc proposed a method of estimating the band gap energy of semiconductors using optical absorption spectra. The Tauc method is based on the assumption that the energy-dependent absorption coefficient (α) can be expressed by the following equation (1).

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \quad \text{..(1)}$$

Where α is the absorption coefficient

h is the planks constant

A is the proportionality constant

E_g is the band gap energy and

γ denotes the nature of the electronic transitions

$\gamma=2$ for direct allowed transitions

$\gamma=1/2$ for indirect allowed transitions

$\gamma=2/3$ for direct forbidden transition

$\gamma=1/3$ for indirect forbidden transition

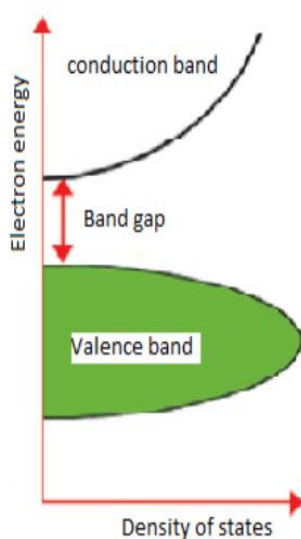


Fig 1. Explanation of Band gap



Fig: 2 UV-VIS Photo spectrometer

Procedure: The determination of band gap energy by using Tauc's plot

1. Plotting the value of $(\alpha h\nu)^2$ with $h\nu$
2. Taking the extrapolation in the linear area across the energy axis in the corresponding graph
3. The intersection with energy-axis is the estimation of the corresponding energy gap

Calculations of α (absorption coefficient) and $h\nu$ (energy)

1. α can be estimated by using formula $\alpha=2.303 \times \text{Absorbance}$ (for liquid sample) and $\alpha=\text{Absorbance}/\text{film thickness}$ (for thin film sample)
2. Energy ($h\nu$) can be calculated by using formula $E= h\nu=hc/\lambda=1240/\lambda$

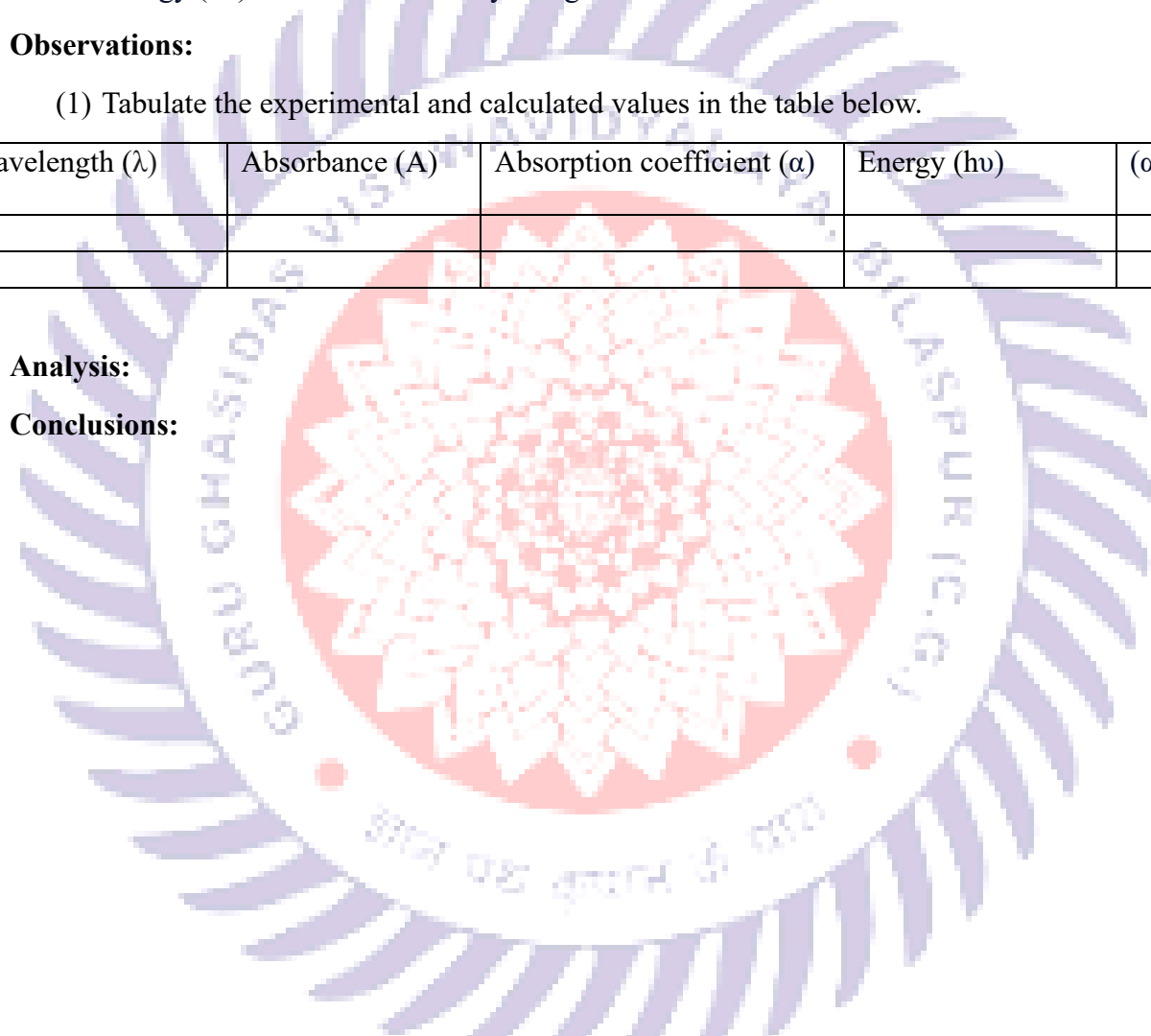
Observations:

(1) Tabulate the experimental and calculated values in the table below.

Wavelength (λ)	Absorbance (A)	Absorption coefficient (α)	Energy ($h\nu$)	$(\alpha h\nu)^2$

Analysis:

Conclusions:



Experiment No 2

Aim: To measure the average crystallite size using XRD data of a given nanomaterial.

Requirements: XRD data of powder sample.

Theory: X-ray diffraction is a convenient method for determining the mean size of nano crystallites in nanocrystalline bulk materials with phase certain. The determination refers to the main peaks of the pattern diffractogram through the approach of Debye Scherrer's equation formulated in Equation. The Scherrer equation, in [X-ray diffraction](#) and [crystallography](#), is a formula that relates the size of sub-micrometre [crystallites](#) in a solid to the broadening of a peak in a diffraction pattern. It is often referred to, incorrectly, as a formula for particle size measurement or analysis. It is named after [Paul Scherrer](#). It is used in the determination of the size of crystals in the form of powder.

The Scherrer equation can be written as:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where:

D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, which may be smaller or equal to the particle size.

K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9 but varies with the actual shape of the crystallite.

λ is the [X-ray wavelength](#).

β is the line broadening at half the maximum [intensity \(FWHM\)](#) as shown in the figure below, after subtracting the instrumental line broadening, in [radians](#).

θ is denoted as Bragg's law.

Procedure:

1. Identify the K value.
2. Identify the λ value.
3. Identify FWHM (β).

To determine the value of FWHM (β) can be done using the following ways:

Step 1: Identify the sharpest peak or crystalline area in the diffraction pattern generated by XRD.

Step 2: Determine the value of 2θ at the peak with the maximum intensity of the XRD diffraction pattern.

Step 3: Determine the value of half of the maximum peak intensity.

Step 4: Determine the minimum 2θ value and the maximum 2θ value at half the maximum intensity of the peak.

Step 5: Determine the FWHM (β) value using Equation $\beta = \frac{1}{2}(2\theta_{max} - 2\theta_{min})$

4. Determine the value of $\cos\theta$ from the value of 2θ value.

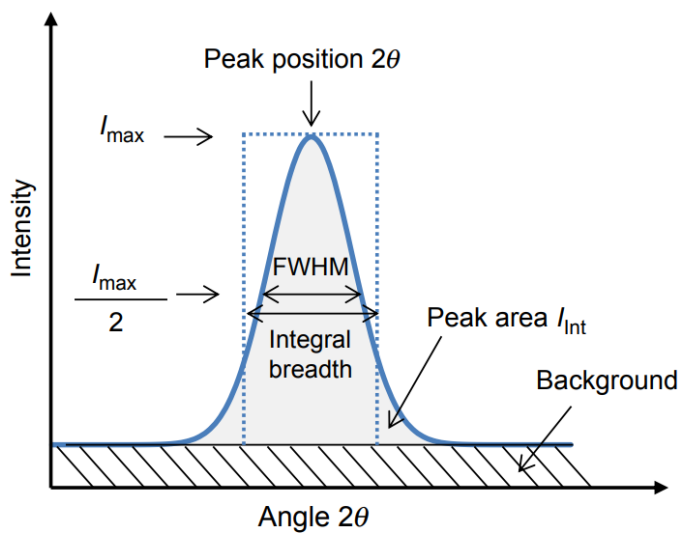
The steps to determine the value of \cos from the value of 2θ are as follows:

Step 1: Divide the value of 2θ theta by the number 2 thus θ is known.

Step 2: Change θ value to $\cos\theta$.

5. After all the values from step 1 to step 4 are known, the last step is to put these values in Equation (1) so that the crystal size is obtained.

In short, by performing a curve selection of the diffraction peaks of each plane crystal at position 2θ , we can see half-peak curve widening value diffraction (FWHM), then with a value of is put into the equation Scherrer to determine the size crystal.



Observations:

1. Tabulate the calculated data for every 2θ in the table below:

2θ	θ	$\cos\theta$

2θ ($^{\circ}$)	$\cos \theta$	K ($\text{rad}/\text{\AA}^2$)	λ (nm)	FWHM β ($^{\circ}$)	FWHM β (rad)	Crystallite Size (nm)

Analysis:

Conclusions:



Experiment No 3

Aim: Estimation of lattice strain in nanoparticle by XRD pattern.

Requirements: XRD data of powder sample.

Theory: Williamson-Hall (W-H) analysis is a simplified integral breadth method where both size-induced and strain-induced broadening are deconvoluted by considering the peak width as a function of 2θ . W-H analysis is employed for estimating crystallite size and lattice strain. The significance of the broadening of peaks evidences grain refinement along with the large strain associated with the powder. The instrumental broadening (β_{hkl}) is corrected corresponding to each diffraction peak XRD pattern using the equation:

$$\beta_{hkl}^2 = (\beta_{hkl})_{\text{Measured}}^2 - (\beta_{hkl})_{\text{Instrument}}^2 \dots (1)$$

The average nanocrystalline size was calculated using Debye-Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos\theta} \dots (2)$$

where D = crystalline size, K = shape factor (0.9), and λ = wavelength of Cu α radiation.

The strain induced in powders due to crystal imperfection and distortion:

$$\epsilon = \frac{\beta_{hkl}}{\tan\theta} \dots (3)$$

From Equations 2 and 3, it was confirmed that the peak width from crystallite size varies as $\frac{1}{\cos\theta}$ strain varies as $\tan\theta$. Assuming that the particle size and strain contributions to line broadening are independent to each other and both have a Cauchy-like profile, the observed line breadth is simply the sum of Equations 2 and 3.

$$\beta_{hkl} = \frac{K\lambda}{D \cos\theta} + 4\epsilon \tan\theta \dots (4)$$

By rearranging the above equation, we get:

$$\beta_{hkl} = \frac{K\lambda}{D \cos\theta} + 4\epsilon \tan\theta \dots (5)$$

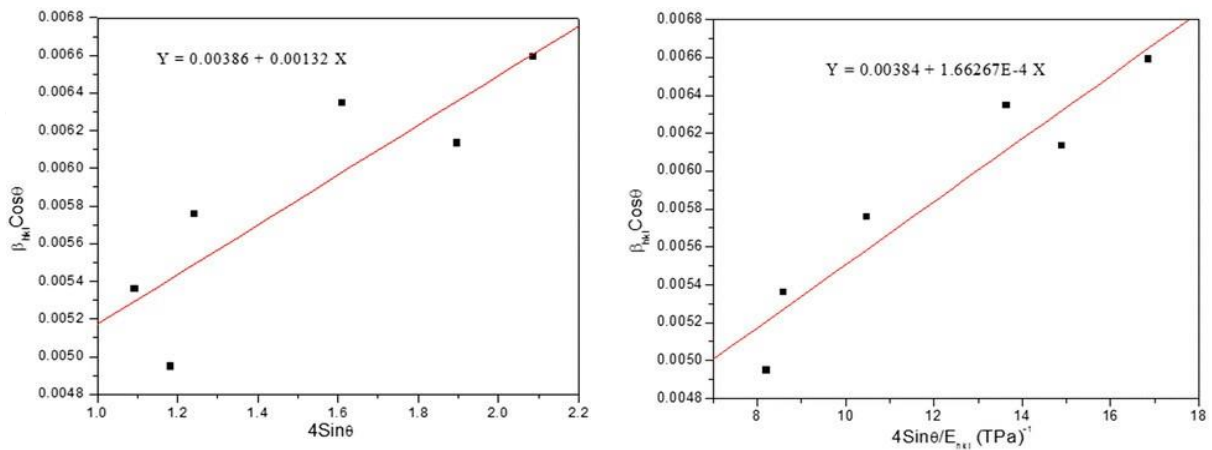
The above equations are W-H equations. A plot is drawn with $4\sin\theta$ along the x-axis and $\beta_{hkl} \cos\theta$ along the y-axis for as prepared samples. From the linear fit to the data, the crystalline size was estimated from the y-intercept, and the strain ϵ , from the slope of the fit.

Uniform deformation stress and uniform deformation energy density were taken into account; the anisotropic nature of Young's modulus of the crystal is more realistic. The generalized

Hook's law referred to the strain, keeping only the linear proportionality between the stress and strain, i.e., $\sigma = E \epsilon$. Here, the stress is proportional to the strain, with the constant of proportionality being the modulus of elasticity or Young's modulus, denoted by E. In this approach, the Williamson-Hall equation is modified by substituting the value of ϵ in Equation 5.

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + \frac{4 \sin \theta \sigma}{E_{hkl}}$$

E_{hkl} is Young's modulus in the direction perpendicular to the set of the crystal lattice plane (hkl). The uniform stress can be calculated from the slope line plotted between $4 \sin \theta / E_{hkl}$ and $\beta_{hkl} \cos \theta$, and the crystallite size D, from the intercept as shown in the figure below.



Conclusions:

Analysis:

Experiment No 4

Aim: To calculate the grain size of a material from SEM micrograph.

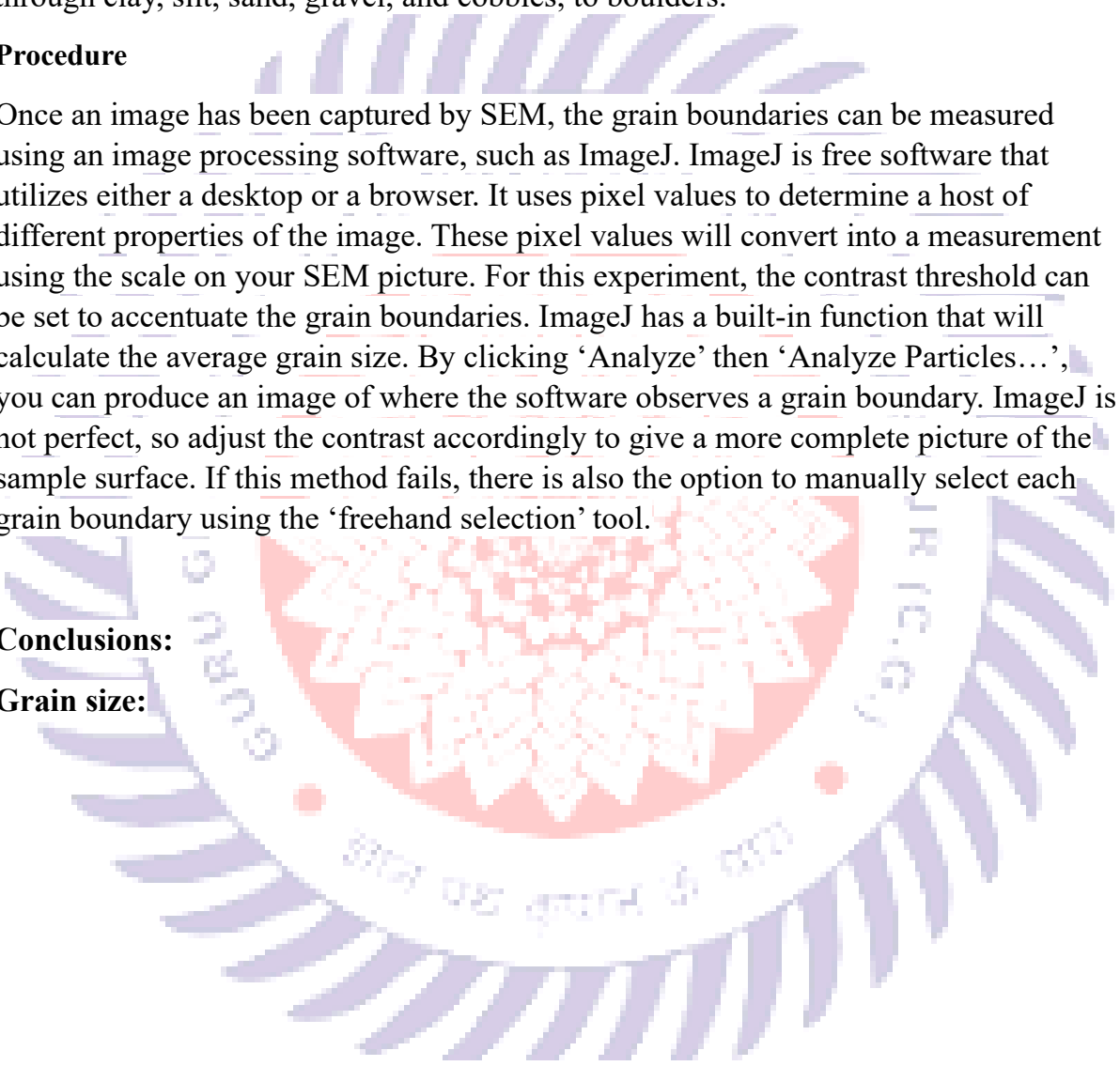
Theory: Grain size (or particle size) is the diameter of individual grains of sediment, or the lithified particles in clastic rocks. The term may also be applied to other granular materials. This is different from the crystallite size, which refers to the size of a single crystal inside a particle or grain. A single grain can be composed of several crystals. Granular material can range from very small colloidal particles, through clay, silt, sand, gravel, and cobbles, to boulders.

Procedure

Once an image has been captured by SEM, the grain boundaries can be measured using an image processing software, such as ImageJ. ImageJ is free software that utilizes either a desktop or a browser. It uses pixel values to determine a host of different properties of the image. These pixel values will convert into a measurement using the scale on your SEM picture. For this experiment, the contrast threshold can be set to accentuate the grain boundaries. ImageJ has a built-in function that will calculate the average grain size. By clicking 'Analyze' then 'Analyze Particles...', you can produce an image of where the software observes a grain boundary. ImageJ is not perfect, so adjust the contrast accordingly to give a more complete picture of the sample surface. If this method fails, there is also the option to manually select each grain boundary using the 'freehand selection' tool.

Conclusions:

Grain size:



Experiment No 5

Aim: To analyse the absorption and emission spectrum of a given material.

Requirements: Uv-Vis spectra and luminescence spectra.

Theory: UV-Visible absorption spectroscopy involves measuring the absorbance of light by a compound as a function of wavelength in the UV-visible range. When a molecule absorbs a photon of UV-Vis light, the molecule is excited from its ground state to an electronic excited state. In other words, an electron is promoted from the HOMO (Highest-energy Occupied Molecular Orbital) of the molecule to the LUMO (Lowest-energy Unoccupied Molecular Orbital) of the molecule. The HOMO is commonly a π orbital of a conjugated functional group and the LUMO is commonly a π^* orbital of the conjugated functional group. The smaller the energy difference between HOMO and LUMO, the less energy is needed and the longer the wavelength that will be absorbed (Figure 1-1).

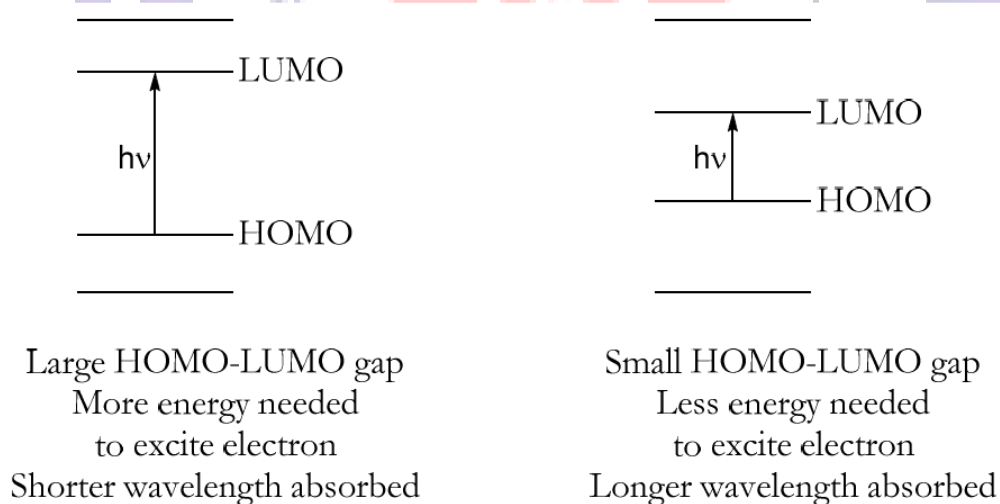


Figure 1-1: The relationship between HOMO-LUMO gap and absorbed wavelength of light

Whenever a compound absorbs a particular wavelength or color from white light, the combination of the reflected wavelengths makes the compound appear a complementary color. For example, if a compound absorbs in the visible region at 590 nm, which is yellow, the combination of all the other wavelengths which are reflected makes the compound appear blue. The exact cutoffs for these color ranges are somewhat subjective, but most reference sources cite values similar to the ones given below.

λ_{\max} (nm)	Color Absorbed	Color Observed
<400	Ultraviolet	White
400–435	Violet	Yellow-Green
435–480	Blue	Yellow
480–500	Green-Blue	Orange

500-560	Green	Red
560-590	Yellow-Green	Violet
590-600	Yellow	Blue
600-610	Orange	Green-Blue
610-700	Red	Green

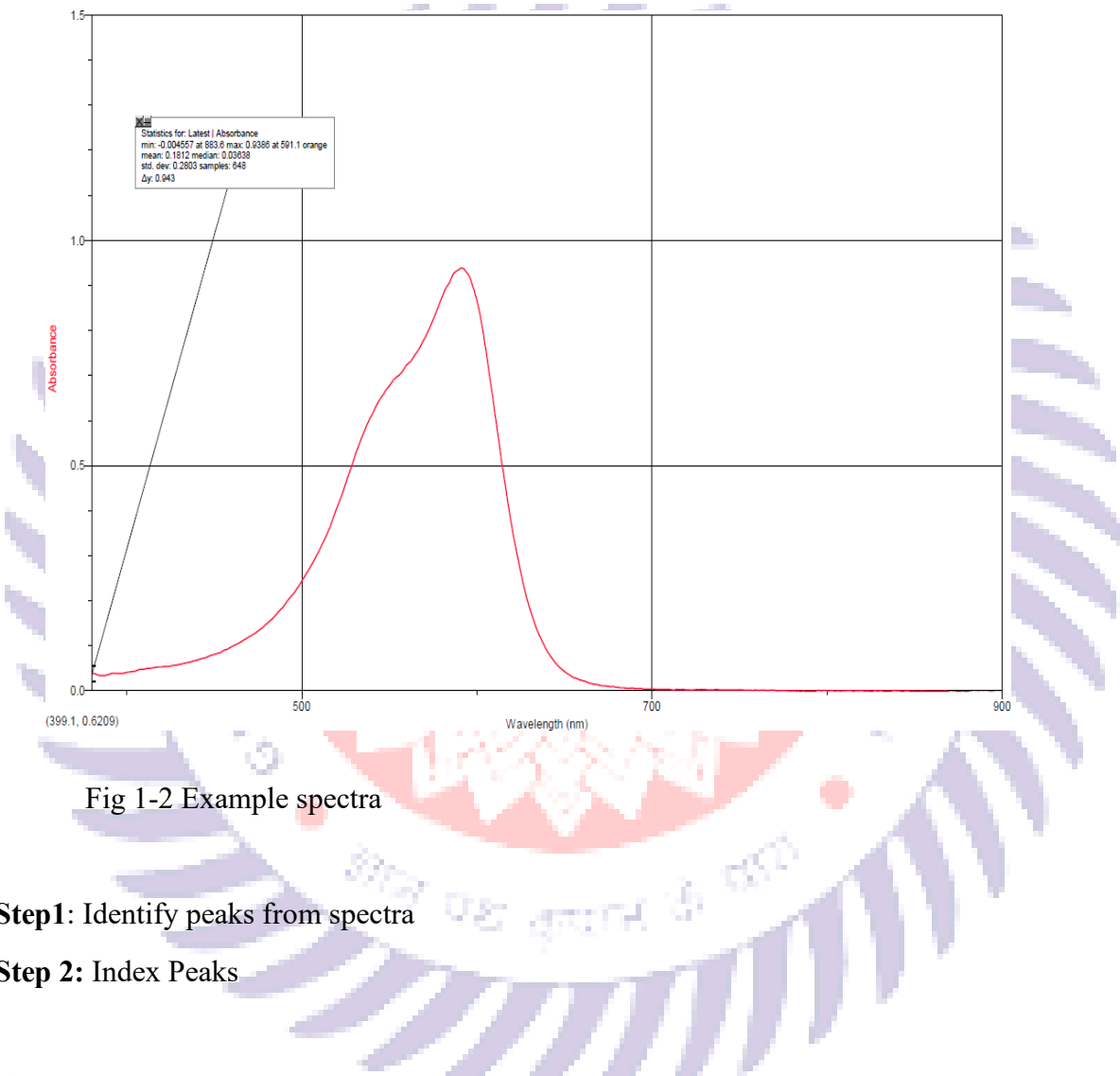


Fig 1-2 Example spectra

Step1: Identify peaks from spectra

Step 2: Index Peaks

Conclusions

Result

Emission Wavelength:

Excitation Wavelength:

Experiment No 6

Aim: Synthesis of nanomaterial by combustion method ZnO/MgO.

Requirements: Precursors, DI water, Magnesium Nitrate or other/Zinc Nitrate or other, Urea, Citric Acid.

Theory: The solution combustion method is a versatile, fast, and economical technique for the synthesis of ceramic oxides. This method involves burning a redox mixture containing the stoichiometric ratio of the oxidizing agent and fuel in a preheated dampening furnace. Combustion is a fast and independent exothermic reaction between metal salts and organic fuels. A large amount of gas is generated during the combustion process to prevent the agglomeration of nanoparticles.

Preparation method

Magnesium nitrate is used as a precursor and urea as a fuel. Magnesium nitrate was dissolved in deionized water and urea as fuel was added to the precursor solution with constant stirring (1000 rpm). solution at $\sim 70\text{--}80^\circ\text{C}$ for 2 hours with continuous stirring. After the gel properties were formed, the dissolution was brought to room temperature, then transferred to a crucible which was placed in a muffle furnace at a temperature of 500°C for 3 hours. Due to heat energy, the combustion reaction occurs between the precursor (oxidizing agent) and urea (fuel). The white powder obtained is then ground using a mortar and pestle. The ground powder will be used for further analysis. In the combustion system, the desired product is prepared from a combustion reaction that takes place spontaneously at a high temperature at a high rate.

The same preparation method can be applied to prepare ZnO nanoparticles too.



Conclusions

Result: Confirm the preparation by indexing XRD with literature.