Chapter – 2

*Synthesis and Characterization Tools of ZnO and Cu Doped ZnO Nanostructures*
2.1. Introduction

Synthesis and processing of nanostructures with high precision is significant to the advancement of nanoscience and nanotechnology. It is well known that properties and applications of nanostructure materials are possible only when they are made with desired size, morphology, and chemical composition [1-8]. Different methods have been used by researchers and scientists for the synthesis of ZnO nanostructures [9-20]. In addition, synthesis of nanostructures by wet chemical method is attractive due to its perfect control of morphology, purity, crystallinity, composition and low cost for large-scale production, and high degree of flexibility. The size and morphology of the nanostructures can be controlled through the manipulation of the experimental conditions such as reaction temperature, pH value of the solution, concentration of the precursors, variation of surfactants/capping agents, doping variation etc.

In the present study, wet chemical method was used for the synthesis of the samples. The methods of preparation of the ZnO and Cu doped ZnO nanostructures for the present study and the details of experimental techniques used for their characterization are presented in this chapter.

2.2. Motivation of Wet Chemical Method

Chemical method is a widely used technique to produce nanostructures due to the advantage of improved compositional homogeneity since the reactant constituents are mixed at a molecular level. Precipitation from aqueous solution is the most commonly used method for preparing nanoparticles. In this method, synthesis system consists of precursors, surfactants and solvents in which nanostructures can be formed by the reduction and decomposition of precursors. There are two important processes that are involved in the growth of nanocrystals from solution- (i) nucleation, and (ii) growth of the nanocrystals. A polymeric surfactants/stabilizer can be used to control the size and distribution of the semiconductor nanoparticles. The polymer is attached electrostatically to the surface of the growing nano clusters, and prevents their further growth.
We have synthesized the ZnO and Cu doped ZnO NPs using wet chemical method because of its-

- Simplicity of fabrication.
- Requirement of inexpensive and simple instruments.
- Relatively shorter synthesis time.
- Possibility of large scale production.
- Possibility of producing single crystalline nanoparticle.
- Possibility of doping of large number of materials even at room temperature.
- Accurate synthesis of nanoparticles in the form of colloids, powders and thin films.

### 2.3. Use of Polyvinyl Pyrrolidone (PVP) as a surfactant

![Figure 2.1 Structure of PVP.](image)

A number of organic materials are used as capping/protective agents for the synthesis of nanoparticles since this is an easy way of stabilizing them to avoid agglomeration [21] and also preventing colloid sintering [22]. In our investigation, polyvinyl pyrrolidone (PVP), a water-soluble polymer has been used as capping molecules and also acts as stabilizer against agglomeration. In the presence of PVP in a solution, both N and C=O groups, has been used as capping molecules and also acts as stabilizer against agglomeration [23]. Synthesis of nanostructures using PVP can form a shell surrounding the particles and prevent them from aggregating to larger particles and grain growth by its steric effect [24]. Beside the steric activity of PVP, it allows the reaction to happen also at room temperature and decreases the particle size. Using PVP as a capping molecule, ZnO nanoparticle
surfaces exhibited enhanced UV photoluminescence and reduced ZnO nanoparticles [25]. This can be attributed to the nearly perfect surface passivation of ZnO nanoparticles by the PVP molecules. Figure 2.1 shows the structure of PVP molecules.

2.4. **Synthesis of ZnO and Cu Doped ZnO Nanostructures**

2.4.1. **Materials**

For synthesis of ZnO nanostructures at various environments, we have used the following materials:

- Zinc nitrate hexahydrate \([\text{Zn(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}]\) from Merck Specialities Private Limited, Mumbai, INDIA.
- Ammonia solution (about 30% GR) from Merck Specialities Private Limited, Mumbai, INDIA.
- Polyvinyl pyrrolidone (PVP, M.W. 40000) from LOBA Cheme, Mumbai, INDIA.
- Copper chloride dehydrate \((\text{CuCl}_2\cdot 2\text{H}_2\text{O})\) from Merck Specialities Private Limited, Mumbai, INDIA.
- Distilled water from Merck Specialities Private Limited, Mumbai, INDIA.
- Filter paper (Cat No 1542 – 125) from Whatman, UK.

All the chemicals were purchased from the commercial market and used without further purification.

The Glassware used during synthesis was purchased from Borosil® Glass Works Limited, Mumbai, INDIA.

2.4.2. **Synthesis of ZnO Nanostructures by Wet Chemical Method**

2.4.2.1. **Synthesis of ZnO nanostructures at different pH**

To synthesize ZnO nanoparticles, 100 ml of 0.1 M solution of \(\text{Zn(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}\) was stirred constantly for 30 min at 60 °C (solution A). 3 wt% of PVP was stirred constantly at 60 °C for 30 min (solution B). Now \(\text{NH}_4\text{OH}\) was slowly added drop by drop into solution A and stirred at room temperature for 15 min and the pH of the solution was continuously measured. When the pH of the
solution is 7.5 and a white solution (solution C) of ZnO is formed and the addition of NH₄OH is stopped. The final mixture (solution B and solution C) is stirred constantly for 1 h at 60°C and allowed to cool down at room temperature till the white precipitate of ZnO is formed. The whole solution is allowed to settle overnight in a dark chamber. Finally, the precipitate is filtrated which is washed with distilled water to dissolve the impurities and dried at 60°C in an oven for 12 h to obtain ZnO nanocrystalline powder [26]. Same procedure has been followed for the preparation of ZnO nanoparticles under pH = 8.0, pH = 8.5 and pH = 9.0 by changing concentration of NH₄OH. The samples named as SZOpH₁ for pH = 7.5, SZOpH₂, SZOpH₃, and SZnOpH₄ for pH = 8.0, pH = 8.5, and pH = 9.0 respectively.

In our study, formation of ZnO has been done via the wet chemical route, by the dehydration of Zn(OH)₄²⁻ or Zn(NH₃)₄²⁺ according to the precursors reactions [27]:

\[
\begin{align*}
\text{Zn(NO}_3\text{)₂·6H}_2\text{O} & \iff \text{Zn}^{2+} + 2\text{NO}_3^{2-} + 6\text{H}_2\text{O} \quad (2.1) \\
\text{NH}_4\text{OH} & \iff \text{NH}_4^+ + \text{OH}^- \iff \text{NH}_3 + \text{H}_2\text{O} \quad (2.2) \\
\text{Zn}^{2+} + 4\text{NH}_3 & \iff \text{Zn(NH}_3\text{)}_4^{2+} \quad (2.3) \\
\text{Zn(NH}_3\text{)}_4^{2+} + 2\text{OH}^- & \iff \text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O} \quad (2.4) \\
\text{Zn}^{2+} + 4\text{OH}^- & \iff \text{Zn(OH)}_4^{2-} \quad (2.5) \\
\text{Zn(OH)}_4^{2-} & \iff \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (2.6)
\end{align*}
\]

2.4.2.2. Synthesis of ZnO nanostructures at different annealing temperatures

To prepare the ZnO nanoparticles at the given condition, similar procedures are adopted as described in section 2.4.2.1. It is followed up by heating the sample SZOpH₁/ SZOA₀ (prepared at 60 °C and pH = 7.5, as mentioned in section 2.4.2.1) in a muffle furnace (Ai 009 MUFFLE FURNACE) for 1 h at temperatures of 200 °C, 300 °C and 500 °C respectively. The same pH value of 7.5 is maintained for the samples named as SZOA₁, SZOA₂, and SZOA₃ for annealed
temperatures 200 °C, 300 °C and 500 °C respectively, whereas unannealed sample named as SZOA₀.

2.4.2.3. Synthesis of ZnO nanostructures at different molar concentration of zinc source

To prepare ZnO nanoparticles at different molar concentration of Zn source, Zn(NO₃)₂.6H₂O are taken at different molarities. For the samples, 0.075 M, 0.1 M, 0.15 M and 0.2 M solutions of Zn(NO₃)₂.6H₂O are stirred constantly at 60°C for 30 min, taken one at a time for solution A and the similar procedures are followed as described in 2.4.2.1. In this case also, the same pH value of 7.5 is maintained for the samples named as SZOM₁, SZOM₂, SZOM₃, and SZOM₄ for 0.075 M, 0.1 M, 0.15 M and 0.2 M solutions of Zn(NO₃)₂.6H₂O respectively.

2.4.2.4. Synthesis of ZnO nanostructures at different amount of capping agent

To prepare ZnO nanoparticles with different amount of PVP capping agent, similar procedure is followed for making the solution A (as described in section 2.4.2.1). One of the samples is prepared without adding the PVP solution. Separately 3 wt%, 5 wt% and 7 wt% of PVP solutions are taken and stirred at 60 °C for 30 min for solutions B (as described in section 2.4.2.1). Then similar steps are followed as mentioned in 2.4.2.1. In this case also, the same pH value of 7.5 is maintained for the samples named as SZOPVP₀, SZOPVP₁, SZOPVP₂, SZOPVP₃, and SZOPVP₄ for without adding PVP, 3 wt%, 5 wt% and 7 wt% of PVP solution respectively.

2.4.2.5. Synthesis of undoped and Cu doped ZnO nanostructures at different molar concentration of Cu source

For the preparation of undoped ZnO nanoparticles, simple wet chemical method described in section 2.4.2.1 is followed (sample named as SZOpH₁), while 100 ml of CuCl₂.2H₂O of 0.0075 M solution was added in the prepared sample and stirred constantly at 60 °C for 3 hrs for preparing 7.5% molar Cu doped ZnO nanoparticles at pH = 7.5. Similarly, 100 ml of CuCl₂.2H₂O of 0.005 M solution and 0.0025 M solution were added and stirred constantly at 60 °C for 3 h to obtain
nanocrystalline 5% molar and 2.5% molar Cu doped ZnO sample respectively. The as prepared samples named as $\text{SZOCu}_0$, $\text{SZOCu}_1$, $\text{SZOCu}_2$, and $\text{SZnOCu}_3$ for undoped ZnO, 7.5% molar Cu doped ZnO, 5% molar Cu doped ZnO and 2.5% molar Cu doped ZnO nanoparticles respectively.

2.5. Characterization Tools

2.5.1. X-ray Powder Diffractrometer (XRD)

**Basic principles and theoretical consideration:**

XRD is an important tool for characterization of materials of powder or solid in material science research. It is used to determine crystal structure, phase identification, purity as well as physical properties of materials. X-rays are electromagnetic radiation of photon energies in the range of 100 eV-100 keV and the energy corresponds to the inter-atomic distance in solids $\sim 12 \times 10^3$ eV. Therefore, XRD is a primary tool for characterization of nanostructures as its wavelength is equivalent to the atomic scale.

![Figure 2.2 Bragg's reflection.](image)

When X-rays impinge upon the atoms in the crystal lattice, and are scattered due to each atom, then each of these atoms acts as a source of scattering. All the lattices of the crystal act as series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum, when X-rays scattered from a crystalline solid can constructively interfere, and produce a diffracted beam. In 1912, W. L. Bragg gave a relationship among the distance between similar
atomic planes \((d, \text{ spacing between consecutive parallel lattice planes})\), twice the angle of diffraction \((2\theta, \theta = \text{angle of incidence or Bragg angle})\), and an integral multiple of the wavelength \((\lambda)\) of the incident X-ray radiation. This relation is called Bragg’s law and is given by [28]

\[
2d \sin \theta = n\lambda \tag{2.7}
\]

where \(n\) is the order of diffraction. Therefore, there are several angles of incidences corresponding to \(n = 1, 2, 3, \ldots \) etc. for fixed values of \(\lambda\) and \(d\). The scattered rays differ in path and hence the phase difference is equal to one wavelength for first order diffraction \((n = 1)\). Hence, in consecutive interference of the rays scattered by all the lattices in all the planes are completely in phase, and reinforce one another to form diffracted beam in the direction shown (Figure 2.2). Therefore, Bragg’s law for first order diffraction is given by

\[
2d \sin \theta = \lambda \tag{2.8}
\]

**Lattice constants:**

In the hexagonal structure, the plane spacing \(d\) is related to the lattice constants \((a, c)\) and the Miller indices \((hkl)\) by the relation [29]

\[
\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \tag{2.9}
\]

Combining equations (2.8) and (2.9), we get

\[
\sin^2 \theta = \left(\frac{\lambda}{2a}\right)^2 \left[\frac{4}{3} (h^2 + hk + k^2) + \left(\frac{l\lambda}{c}\right)^2\right] \tag{2.10}
\]

**Special cases:**

(i) XRD peaks for which \(l = 0\) (i.e. \(hkl\) peaks).

(ii) XRD peaks for which \(h = k = 0\) (i.e. \(00l\) peaks).

Applying the above special cases in equation (2.10), we obtain the following equations for lattice constants \((a, c)\).

\[
a = \frac{\lambda}{\sqrt{3} \sin \theta} \sqrt{\left(h^2 + hk + k^2\right)} \tag{2.11}
\]

\[
c = \frac{\lambda}{2 \sin \theta} l \tag{2.12}
\]

For an ideal hexagonal wurtzite lattice [30],

\[
c = (1.6333) a \tag{2.13}
\]

[39]
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Using equations (2.11), (2.12) and (2.13), we can find out the lattice constants \((a, c)\) only which obey the aforesaid special conditions for those \(hkl\) indices.

**Unit cell volume:**

The volume of the unit cell for hexagonal system is given by [29]

\[
V = \frac{\sqrt{3}}{2} a^2 c = 0.866a^2 c
\]  
(2.14)

**Bond length:**

The bond length is given by [31]

\[
L = \sqrt{\frac{a^2}{3} + c^2 \left(\frac{1}{2} - u\right)^2}
\]  
(2.15)

where the positional parameter \(u\) for wurtzite structure is given by

\[
u = \frac{a^2}{3c^2} + 0.25
\]  
(2.16)

**Crystallite size and strain:**

XRD profile analysis is a powerful method to evaluate the broadening of peak with crystallite size and strain due to imperfections within the crystal lattice such as vacancies, dislocations, stacking faults and others. It is well known in powder diffraction pattern that the peaks become broader as \(2\theta\) increases. The broadening of peaks is a combination of both sample- and instrument- dependent effects. To remove these factors, the diffractometer is calibrated prior to XRD observation by a standard material such as silicon (Si), and correction of instrumental broadening of \(\beta_{2\theta}\) arising due to slit width of the \(K\alpha_1\) and \(K\alpha_2\) lines are also made. The diffraction broadening only due to grain size \(\beta_g\) is given by the Warren rule [32]

\[
\beta_g^2 = \beta_{2\theta}^2 - \beta^2
\]  
(2.17)

where \(\beta\) is full width at half maximum (FWHM) of a line produced under similar geometrical conditions by a standard material Si. The crystallite size \((D)\) is then evaluated for the preferred planes \((hkl)\) using Debye Scherrer formula [33]

\[
D = \frac{k\lambda}{\beta_g \cos \theta}
\]  
(2.18)
where $\lambda$ is the wavelength of radiation used, $\theta$ is the Bragg angle (in degrees), $\beta_g$ is the instrumental corrected FWHM (in radians), and $k$ is shape factor (0.9). The broadening of peaks due to strain arising from crystal imperfections and distortion are related as [34]

$$\varepsilon = \frac{\beta_s}{4 \tan \theta}$$  \hspace{1cm} (2.19)

where $\beta_s$ is the strain induced line broadening and $\varepsilon$ is the strain.

From equations (2.18 and 2.19), it is seen that the peak broadening varies as $1/\cos \theta$ and strain varies as $\tan \theta$. Williamson and Hall gave a method for these distinct $\theta$ dependencies for the size and strain broadening by looking at the peak width as a function of $2\theta$[35] and can be expressed as

$$\beta_{hkl} = \beta_g + \beta_s = \frac{k \lambda}{D \cos \theta} + 4 \varepsilon \tan \theta$$  \hspace{1cm} (2.20)

or, by rearranging

$$\beta_{hkl} \cos \theta = \frac{k \lambda}{D} + 4 \varepsilon \sin \theta$$  \hspace{1cm} (2.21)

The above equation (2.21) is known as Williamson-Hall equation, which assumed the strain is uniform in all crystallographic diffractions and represents uniform deformation model (UDM). In UDM model, crystal is considered as isotropic in nature and all the properties of materials are independent of the direction along which they are measured. Williamson-Hall plot (W-H plot) is drawn with $4\sin \theta$ along the $x$-axis and $\beta_{hkl} \cos \theta$ along the $y$-axis for the preferred planes ($hkl$), the value of crystallite size ($D$) is estimated from the $y$-intercept and the slope of the linear fit gives the value of the strain ($\varepsilon$).

**Experimental:**

Powder X-ray diffraction (XRD) pattern of prepared ZnO nanostructures were recorded by Philips X-ray Diffractrometer (X’Pert Pro) with Cu $K_{\alpha}$ radiation ($\lambda = 1.5406$ Å). Here XRD was done by the X-ray diffraction of the as-prepared powder samples using the Diffractometer. In order to identify the phase and to know the structure of ZnO and Cu doped ZnO nanostructures, X-ray diffraction
pattern was recorded in the range of 25° - 75° (2θ) at a scanning rate of 0.02°/s and 0.5 sec/step.

2.5.2. Scanning Electron Microscopy (SEM) with Energy Dispersive Analysis of X-rays (EDAX)

Scanning electron microscope (SEM)

Basic principles:

The scanning electron microscopy (SEM) helps in the study of surface morphology of a specimen. The electrons are produced by thermionic process in a Cathode Ray Tube (CRT) by electric field and are focused onto the specimen. The electrons interacts with atoms of the specimen produces signals containing the information about the surface topography, its chemical compositions and other physical properties [36, 37].

In the interactions, secondary electrons, backscattered and diffracted electrons are also produced. In this microscopy, the secondary and back scattered electrons are employed to serve the purpose. It also has very large resolution, where the very close images can be resolved and magnified. In SEM, the depth of field is very large, for which at a time more than one specimen can be placed and focused.

Energy dispersive analysis of X-rays (EDAX)

Energy dispersive analysis of X-ray (EDAX) is a technique used for the analysis and characterization particularly elemental and chemical analysis of a specimen. It is one of the most variants of X-ray fluorescence spectroscopy which is employed on the investigation of a specimen through interactions between electromagnetic radiation and matter. It analyzes X-rays emitted by the matter in response to it being impinged with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element’s atomic structure to be identified uniquely from one another. A high energy beam of charged particles such as electrons or a beam of X-rays is focused onto the sample taken to be studied to stimulate the emission of characteristic X-rays from a specimen. At rest, an atom within the sample contains ground state (or
unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell, creating an electron-hole pair. An electron from an outer and higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured [38, 39].

**Experimental:**

Morphological and elemental investigations were carried out with SEM/EDAX (JEOL, JSM-6390 LV and JSM-6360). The samples were prepared by adhering with a small amount of the powder sample onto a copper stub using double-sided carbon tape. The as prepared samples were then sputtered with gold to reduce charging effect during the measurement.

**2.5.3. Transmission Electron Microscopy (TEM)**

**Basic Principles:**

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons are made to bombard with an ultra thin specimen so as to interact with it. As a result, the interaction carries information in terms of images, which are magnified and are made to form imaging devices.

It is based on the principle of light microscope. In this case, electrons are used instead of light to make better resolution and it is much larger than that of light microscope. The electrons are emitted by thermionic process in CRT, which are accelerated by an electric field and are focused onto the specimen by electric and magnetic fields. The electrons in the outgoing beam can be detected by using a photographic film, or fluorescent screen such that in areas where electrons are scattered appear dark on the screen, or on a positive image [40].

[43]
Owing to its large magnification, it is of great use in research work particularly in biological and material science. Transmission electron microscopy is a straightforward technique to determine the size and shape of the nano and micro sized materials as well as to obtain structural information. The contrast of TEM images at smaller magnifications is due to absorption of electrons in the specimen at the smaller magnifications. At higher magnifications, complex wave interactions modulate the intensity of the image.

High-Resolution Transmission Electron Microscopy (HRTEM) is a powerful tool for studying the structure of particles, interfaces and crystal defects. It provides highest resolution of about 0.08 nm with microscopes [41]. Because of this high resolution, this unique tool helps to study the properties of nanocrystalline materials like semiconductors and metals. The phase-contrast imaging is the basis of image formation in HRTEM. In this type of imaging, the contrast may not be interpretable spontaneously because the image is affected by aberrations of imaging lenses.

**Selected area electron diffraction pattern (SAED)**

SAED is an optional arrangement in HRTEM. This is a unique electron diffraction capability to generate images of different contrast, and also for crystal structure analysis of individual nonmaterial of the different parts of a sample. A small area can be selected from a high resolution transmission image of a sample and generate its electron diffraction pattern (rings or spots) produced on the screen. The SAED allows determining the lattice constant of the crystalline material that can help in identification of species. The diffraction patterns are basically distinguishable as spot patterns resulting from single crystal diffraction zones or ring patterns are obtained from the randomly oriented crystal aggregates (polycrystalline).

The basic equation for electron diffraction of TEM is given by [42]:

\[ Rd = L\lambda \]  

(2.22)

where \( R \) is the distance from the centre of a standard electron diffraction pattern to a diffraction spot, \( d \) is the interplanar spacing, \( L \) is the effective camera length of a
TEM ($L = 1.0 \text{ m for a TEM operating at 200 kV accelerating voltage}$), and $\lambda L$ is termed as the camera constant of TEM ($\lambda = 0.00251 \text{ nm, the wavelength of electrons for 200 kV}$). In the present work, TEM (JEM-2100, JEOL) operating at an accelerating voltage of 200 kV was used for the confirmation of the formation of nanostructures.

**Experimental:**

TEM were carried out on a JEM-2100, JEOL operated at 200 kV. The specimens for the TEM/HRTEM/SAED study were prepared by suspending solid samples (powder) in distilled water. A small amount of sample was added to 4-5 mL of distilled water in a small glass vial, followed by sonication for 15 min in an ultrasonic water bath. The well-dispersed suspension was then dropped onto a carbon-coated copper grid, followed by drying under ambient condition before it was placed in the sample holder of the microscopes.

**2.5.4. Ultraviolet-visible (UV-vis) Absorption Spectroscopy**

**Basic principles and theoretical consideration:**

UV-vis absorption spectroscopy is an important characterization technique to examine the optical properties of materials and semiconductors. The UV-vis spectrometer is based on the fact that molecules of the sample absorb UV or visible light, which results in the excitation of outer electrons in the molecule. The measurements can be done by a monochromatic wavelength or a wide spectral range. The characteristics of chemical structure of a sample are the wavelength of the light absorbed by the sample. Different types of molecules of a sample absorb different spectral regions in the UV-vis spectrum. UV-vis absorption can result in transition of electrons to higher energy states and each molecule undergoes electronic excitation following absorption of light. The study of the absorption spectra helps to identify atomic and molecular species, since they are characteristic of molecular structure [41]. Optical absorption has been used to measure the absorption of interband transition energies in semiconductors [43]. The size dependent properties can also be observed in UV-vis absorption spectrum, particularly in the nano and atomic scales.
The band gaps between the lowest conduction band (LUMO) and the highest lying valence band (HOMO) in a bulk semiconductor can be described as continuum as the energy levels are so close together and result in broad peaks. However, on the nanoscale the band gaps are discrete as they have a small and finite distance between them, meaning that their absorption and emission peaks will be sharp. Due to the discrete energy levels in semiconductor nanostructures the photon energy can be accurately determined and used to measure the band gap energy of a semiconductor.

The energy gap between valance band (the highest energy band occupied by electrons) and conduction band (the lowest unoccupied band) is called band gap energy ($E_g$). When a photon of energy is equal or more than $E_g$ is absorbed in a semiconductor, an electron-hole pair ($e^- - h^+$) will be created which results in absorption of light i.e. absorption of light occur in a semiconductor when the energy of a quantum is greater than $E_g$ and is given by

$$E_g = h\nu = \frac{hc}{\lambda_0} = \frac{1240}{\lambda_0 \text{(in nm)}} \text{ eV}$$

(2.23)

where $h =$ Planck's constant $= 6.626 \times 10^{-34}$ Js,

$c =$ velocity of light $= 3 \times 10^8$ ms$^{-1}$,

and $\lambda_0 =$ absorption wavelength.

Experimentally, the absorption wavelength ($\lambda_0$) is determined at that point from the plot drawn with wavelength ($\lambda$) along x-axis and absorbance ($A$) along y-axis where there is an abrupt change in absorbance. For bulk ZnO, $\lambda_0 \sim 376$ nm gives $E_g \sim 3.3$ eV at room temperature 300 K [44].

The relation between the intensity of incident light ($I_0$) to the intensity of transmitted light ($I$) through a solution of an absorbing material is given by

$$A = - \log_{10} \left( \frac{I}{I_0} \right) = \varepsilon cl = al$$

(2.24)

where $\varepsilon =$ molar absorptivity (extinction coefficient),

[46]
$c = \text{concentration of absorbing species of the absorber,}$

$l = \text{distance light travels through the material i.e. the path length,}$

and $\alpha = \text{absorption coefficient of the substance.}$

The above equation (2.24) is known as Beer-Lambert law [41, 45].

**Optical band gap:**

The interband absorption theory shows that near optical band edge, the absorption coefficient ($\alpha$) is related to the photon energy ($h\nu$) by

$$\alpha h\nu = k(h\nu - E_g)^m$$  \hspace{1cm} (2.25)

where $k$ is a constant and $E_g$ is the band gap energy of the material. For a direct transition, like ZnO (in our case), $m = \frac{1}{2}$.

Thus for direct transition, the above equation (2.25) can be written as

$$(\alpha h\nu)^2 = k(h\nu - E_g)$$ \hspace{1cm} (2.26)

When a plot is drawn taking ($h\nu$) along x-axis and $(\alpha h\nu)^2$ along y-axis for absorption coefficient ($\alpha$), the value of $E_g$ can be determined from the extrapolation of the linear part of the curve $(\alpha h\nu)^2 = 0$ [46].

**Experimental:**

UV-vis absorption spectra were measured on UV-vis spectrophotometers (Shimadzu UV-1800). A small amount of sample was first dispersed in distilled water. The as-prepared nano solution was then transferred into a 10 mm (1 cm) sampling quartz cuvette for analysis, using distilled water as reference.

**2.5.5. Photoluminescence (PL) Spectroscopy**

**Basic principles:**

Photoluminescence is the light emission from substance under examination, when it is being collided with photons of suitable wavelength usually from
monochromatic source (LASER) having energy above the band gap of the sample. As a result, the substance absorbs them and hence electronic excitation takes place i.e. the charge carriers are excited from valence band to conduction band. The electrons are excited, relaxed and then returned to the ground state when recombination takes place. These light emitted with frequency equal to the band gap of the sample are called Photoluminescence. The emitted light is analyzed to get the characteristic property of radiative and non-radiative excitations of the substance. The PL spectrum gives the transition energies, energy levels and further investigations give the underlying bands in minuscule scale [47]. The Photoluminescence technique is a simple method for obtaining the optical properties and electronic structure of semiconductors and for its simplicity it is best used as characterization tool.

**Experimental:**

PL spectra were measured on Fluorescence Spectrometer (HITACHI–2500) at room temperature. A small amount of sample was first dispersed in distilled water. For analyzing, as-prepared nano solution was then transferred into a 1 cm sampling quartz cuvette.

**2.5.6. Fourier Transform Infrared (FTIR) Spectroscopy**

**Basic principles:**

FTIR Spectroscopy is the technique used for determining the chemical bonding and atomic structure of an organic or inorganic material. It is an easy method of analyzing infrared rays, which ranges from $300 \times 10^9$ Hz to $340 \times 10^{12}$ Hz. When infrared rays are incident onto a substance, molecular vibrations occur. The substance absorbs energy corresponding to its characteristic frequency and transmits energies for all the remaining frequencies. The resulting spectrum consists of absorption peaks, corresponding to the frequencies of vibrations between the molecular bonds. The analysis of the absorbed energy determines the functional group of the molecules. The plot between the absorbed energy and the frequency is called the infrared spectrograph. Different materials have different infrared spectra and hence different functional groups or chemical compositions. Clearly, IR spectra provide the qualitative analysis of materials. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The sample's
transmission coefficient and reflection coefficient of the infrared rays at different frequencies is translated into an IR absorption spectrum consisting of reverse peaks. FTIR spectroscopy does not require a vacuum, since neither nitrogen nor oxygen gases absorb infrared rays. FTIR analysis can be applied to minute quantities of materials, whether solid, liquid, or gas. In some cases, if the library of FTIR spectral patterns does not provide an acceptable similarity, then individual peaks in the FTIR plot may be used to yield partial information about the sample. Some software based IR spectroscopes are used as an excellent tool for quantitative analysis of materials. Radiation source, monochromator and detector are the main components of IR spectrometer. Generally an electrically heated inert solid (1000-1800 °C) is used as the radiation source [41]. The monochromator disperse the wide spectrum of radiation and offers IR radiation of suitable frequency range. For this, a combination of prisms or gratings with variable slit mechanisms, mirrors and filters are used. Photon detectors, like thermocouples, thermistors and Golay detectors are the two usual types of IR detectors used in IR spectrometer. Thermal detectors measure the heating effects generated by IR radiation.

Fourier Transform Spectrometers have superior speed and sensitivity as compared to dispersive instruments for most applications. In FTIR spectroscopy, all component frequencies are viewed simultaneously. All molecules absorb IR light except monoatomic and homopolar diatomic molecules. Molecules only absorb some IR radiations, whose frequencies affect the dipole moment of the molecule. The dipole moment of a molecule is due to the differences of the charges in the electronic fields of its atoms. Molecules having only a dipole moment interact with infrared photons. The interaction can result in the excitation of molecules to higher vibrational states. The electronic fields of atoms of homopolar diatomic molecules are equal and hence, they do not possess a dipole moment. No dipole moment is associated with monoatomic molecules also because they have only one atom. Since monoatomic and homopolar diatomic molecules have no dipole moments, they do not absorb IR radiation. It has also overcome the slow scanning process and individual measurement of energy absorbed by the
molecules. Different interferometers are used to get the interferogram, where the energy absorbed by different molecule is encoded. The required information can be extracted by decoding the interferogram using FTIR.

**Experimental:**

Information of chemical bonding on as prepared ZnO and Cu doped ZnO nonmaterials were studied using the potassium bromide (KBr) pellet technique by PerkinElmer Fourier transform infrared spectrometer (Spectrum Two). A small amount of prepared samples were mixed with KBr powder in a ratio of 1:10 for making KBr pellets. The FTIR spectrum was collected from 400 to 4000 cm\(^{-1}\) at 200 scans with a resolution of 4 cm\(^{-1}\).

**2.6. Conclusion**

1. We have synthesized ZnO nanostructures using Zn(NO\(_3\))\(_2\).6H\(_2\)O and NH\(_4\)OH as precursors in distilled water with PVP as a capping agent by a simple wet chemical method.
2. Cu doped ZnO nanostructures were synthesized using Zn(NO\(_3\))\(_2\).6H\(_2\)O, NH\(_4\)OH, and CuCl\(_2\).2H\(_2\)O as precursors in distilled water with PVP as a capping agent by a simple wet chemical method.
3. The undoped ZnO nanostructures appear white in colour, whereas Cu doped ZnO nanostructures for different molar concentrations of Cu source become light blue, and the colour becomes deep blue with increasing Cu concentration.
4. It has also been observed in synthesized samples, sample SZnOA\(_2\) appears light grayish black colour annealed at 300 °C, and sample SZnOA\(_3\) appears deep grayish black colour annealed at 500 °C.

**2.7. References**


Chapter - 2  Synthesis and Characterization Tools of ZnO and Cu Doped ZnO Nanostructures


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[21]. C. J. Murphy, Appl. Spectrosc. 56, 16A (2002).


Chapter - 2  Synthesis and Characterization Tools of ZnO and Cu Doped ZnO Nanostructures


[45]. http://www.chemguide.co.uk/analysis/uvvisible/beerlambert.html


[53]