A Thesis

On

PREPARATION AND CHARACTERIZATION OF Ni-DOPED ZnS NANOPARTICLES FOR DIFFUSE REFLECTANCE

Submitted in the partial fulfilment of requirement for the award of the

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Dedicated

to all

who helped me

throughout my studies

Certificate

This is to certify that report entitled "**PREPARATION AND CHARACTERIZATION OF Ni-DOPED ZnS NANOPARTICLES FOR DIFFUSE REFLECTANCE**" submitted by Simanpreet Kaur, Roll No. 300804020, student of M.Sc. (Physics), Thapar University, Patiala, was carried out by her under my supervision. She has not submitted this material for the credit towards any other degree at Thapar University, Patiala or at any other university.

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Abstract

ZnS nanoparticles doped with Ni were successfully synthesized by chemical precipitation method. The influence of various reaction conditions and dopant concentrations on the formation, phase, morphology and diffuse reflectance of NPs have been investigated and discussed. XRD studies clearly showed the formation of zinc blende phase of ZnS and also confirm that Ni atoms are not incorporated into the lattice of ZnS as no impurity peak of Ni was found. But broadening in the diffraction peaks with different molar concentrations of Ni suggests the presence of Ni on the surface of ZnS. The average crystallite size decreases as the concentration of dopant was increased. TEM micrograph showed the uniformity in shape of synthesized nanoparticles. From the absorption spectra the band gap of the NPs was calculated and found to be higher than that of the bulk counterpart. Also, UV-visible studies showed that band gap of ZnS increases as the concentration of dopant increases. The luminescence property of the NPs was studied by the emission spectrum, which confirms the presence of defect levels caused by the S^{2-} vacancies. PL studies showed that Ni acts as electron trapping center, which results into nonradiative recombination thereby decreasing the luminescent intensity due to S^{2-}. From the reflectance spectra of NPs diffuse reflectance comes out to be 92-98% in the visible region.

Contents

Chapter 1

Introduction

1.1 Nanotechnology

1.1.1 Introduction to Nanotechnology:-

Imagine being able to observe the motion of a red blood cell as it moves through your vein, or being able to watch as a type of white blood cell (called a "T-cell") destroys an invading microbe by engulfing it. What would it be like to observe the vibration of molecules as the temperature rises in a pan of water? To observe sodium and chlorine atoms as they get close enough to actually transfer electrons and form a salt crystal? New scientific tools, developed and improved over the last few decades, make such observations increasingly feasible. These are examples of the effort to view measure and even manipulate materials at the molecular or atomic scale - the major focus of nanotechnology [1].

Nanotechnology is defined as the study and use of structures between 1 nanometer and 100 nanometers in size. Nanotechnology is concerned with materials and systems whose structure and component exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes because of their nanoscale size. Structural features in the range of $\sim 10^{-9}$ to 10^{-7} m (1 to 100 nanometers) determine important changes as compared to the behavior of isolated molecules (1 nanometer) or of bulk materials. More generally, nanotechnology can be defined as any technique able to work at a submicron scale [2]. It is an interdisciplinary science involving physics, chemistry, biology, engineering, material science, computer science etc.

The word nano is from the Greek word ‘Nanos’ meaning dwarf. It is a prefix used to describe "one billionth" of something, or 0.000000001. One nanometer is one billionth of a meter (10^{-9} m). One nanometer is 10-15 hydrogen atoms next to each other. A human hair is about 50,000 - 100,000 nanometers across [3].

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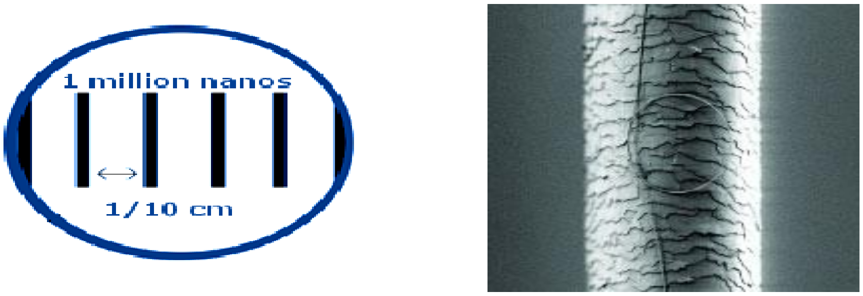


Fig. 1.1 Comparison of nm scale with cm scale and a micrograph shows a nanowire curled into a loop in front of a human hair.

1.1.2 Nanotechnology in nature:-

There are lots of nano materials in nature. Natural processes, such as sea spray and erosion can also create nanoparticles. Nature is expert in fabricating organic structures at the nano scale. Best and most known example of a self cleaning surface is the so called lotus effect. Lotus leaves in particular have the unique ability to avoid getting dirty. Lotus blossoms (the easiest to clean) are coated with tiny hydrophobic particles. When water contacts these particles, it does not wet the leaves. Instead, it simply rolls off, taking with it any dirt in its path. The human body uses natural nanoscale materials, such as proteins and other molecules, to control the body's many systems and processes. For example hemoglobin, which carries oxygen through the bloodstream, is 5 nm in diameter [4].

1.1.3 History:-

Humans have unconsciously used nanotechnology for thousands of years, for example in making paintings. Nanoscale gold was used in stained glass and ceramics in the 10th Century.

Some of the distinguishing concepts in nanotechnology were mentioned by J. C. Maxwell in 1867 when he proposed a thought experiment of a tiny entity known as Maxwell's Demon which is able to handle individual molecules.

Fig. 1.2 Window exhibits red color because of doping with gold nanoparticles and Chinese ruby color pottery using gold particles.

The first observations and size measurements of nano-particles were made during the first decade of the 20th century. Richard Adolf Zsigmondy made a detailed study of gold sols and other nanomaterials with sizes down to 10 nm and less. He published a book in 1914. He used ultramicroscope that employes the dark field method for seeing particles with sizes much less than light wavelength. Zsigmondy was also the first person who used nanometer explicitly for characterizing particle size. He determined it as 1/1,000,000 of millimeter. He developed the first system classification based on particle size in the nanometer range. In the early 1950s, Derjaguin and Abrikosova conducted the first measurement of surface forces [5].

The amount of space available to us for information storage (or other uses) is enormous. As first described in a lecture titled, “There's Plenty of Room at the Bottom” in 1959 by Richard P. Feynman, there is nothing besides our clumsy size that keeps us from using this space. In his time, it was not possible for us to manipulate single atoms or molecules because they were far too small for our tools. Thus, his speech was completely theoretical and seemingly fantastic. He described how the laws of physics do not limit our ability to manipulate single atoms and molecules. However, he correctly predicted that the time would come in which atomically precise manipulation of matter would inevitably arrive [6].

The term 'nanotechnology' was used first by the Japanese scientists Norio Taniguchi (1912-1999) in a 1974 paper on production technology that creates objects and features on the order of a nanometer.

The American engineer K. Eric Drexler (b. 1955) is credited with the development of molecular nanotechnology, leading to nanosystems machinery manufacturing.

The invention of scanning tunneling microscope in the 1980s by IBM Zurich scientists and then the atomic force microscope allowed scientists to see materials at an extraordinary atomic level. These studies provided insight into nanoscale material structures and their properties.

Another breakthrough came in 1985 with the discovery of new shapes for molecules of carbon, known as the buckyball, which are round and consist of 60 carbon atoms. This led to the discovery of a related molecular shape known as the carbon nanotube in 1991. Carbon nanotubes are still one of the most promising areas of nanotechnology as they are about 100 times stronger than steel but just a sixth of the weight; they have unusual heat and conductivity characteristics.

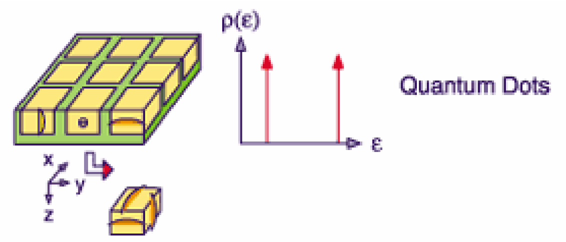
In the late 1990s and early 2000s almost all industrialized nations created nanotechnology initiatives, leading to a worldwide proliferation of nanotechnology activities [7].

1.1.4 Applications of nanotechnology:-

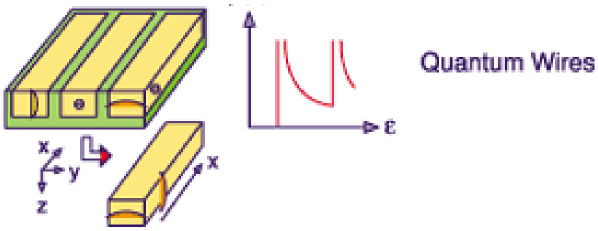
The emerging field of nanoscience and nanotechnology is leading to a technological revolution in the new millennium. Nanotechnology found applications in areas such as medicine, electronics, space, food, fuel cells, solar cells, batteries, fuels , better air quality, cleaner water, chemical sensors, sporting goods, fabric etc [8].

1.1.5 Types of nanomaterials: - Nanomaterials can be characterized into three types [9]:-

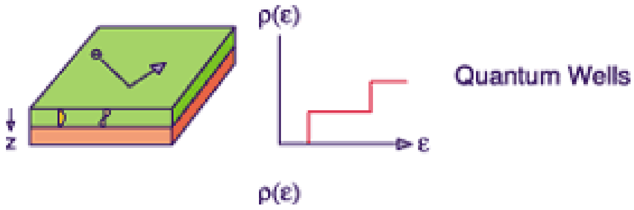
1) Nanoparticles:-Nanoparticles have all of their three dimensions within the nanoscale.



2) Nanotubes: - These can have a diameter that's of nanosize, but can be several hundred nanometers (nm) long or even longer.



3) Nanofilms or nanoplates**:** - These have a thickness that's of nanosize, but their other two dimensions can be quite large.



1.1.6 Changes at nanoscale:-

- **Higher surface area to volume ratio: -** At nanoscale surface area to volume ratio increases. For example Surface area of a sphere is given by = $4\pi r^2$

  Volume is given by = $(4/3)(\pi r^3)$

  Therefore ratio of surface area to volume is= $4\pi r^2 / [(4/3)(\pi r^3)]$

  $=3/r$

  This ratio increases as r decreases. It can be shown by taking examples of spheres of different radius as shown in the table:-

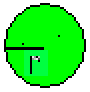
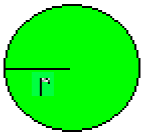
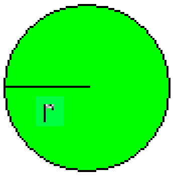
Sphere	Radius R	Surface area to volume ratio (3/r)
	1m	3
	2m	1.5
	3m	1
	4m	.75

Fig. 1.3 Surface area to volume ratio increases as radius of sphere decreases.

- **Dominance of electromagnetic forces: -** Gravitational force is a function of mass and distance and is weak between (low-mass) nanosized particles. Electromagnetic force is a function of charge and distance and not affected by mass, so it can be very strong even when we have nanosized particles. The electromagnetic force between two protons is 1036 times stronger than the gravitational force [10].

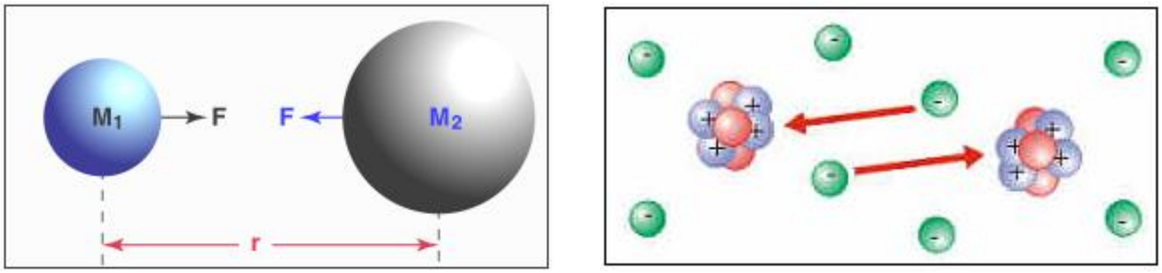


Fig. 1.4 Gravitational force depends on masses and electromagnetic forces depend on charges.

- **<u>Importance of quantum mechanical models: -</u>** Classical mechanical models explain phenomena well at the macroscale level, but they break down when dealing with the very small (atomic size, where quantum mechanics is used) or the very fast (near the speed of light, where relativity takes over). For objects, which are much larger than atoms and moves much slower than the speed of light, classical models do an excellent job. Nanosystems are not large enough for many classical laws of physics to apply. For example, Ohm's law, which describes the relation between current and voltage in a conductor, does not describe current conduction through a tiny nanowire. Here quantum mechanical effects are more important. At the nanoscale there are many phenomena that cannot be explained by classical mechanics. The following are among the most important things that quantum mechanical models can describe (but classical models cannot):
    - Discreteness of energy
    - The wave-particle duality of light and matter
    - Quantum tunneling
    - Uncertainty of measurement

- **<u>Random (Brownian) motion</u>: -** Random molecular motion is the movement that all molecules in a substance exhibit (assuming the sample is above absolute zero) due to their kinetic energy. This motion increases at higher temperatures (temperature is actually a macroscale measure of the average kinetic energy of all the particles in a substance). This motion can involve molecules moving around in space, rotating around their bonds, and vibrating along their bonds. While random kinetic motion is always present, at the macroscale this motion is very small compared to the sizes of the objects and thus is not very influential in how object behave. At the nanoscale however, these motions can be on the same scale as the size of the particles and thus have an important influence on how particles behave. An example of how random kinetic motion can influence things is Brownian motion. Brownian motion is the random movement of tiny particles suspended in a gas or a liquid resulting from bombardment by the fast moving particles of the gas or liquid. Think of a regular submarine in the ocean, even though it is constantly bombarded by the random kinetic motion of the water particles, it is so large that this does not significantly affect its motion through the water. Compare this to the imaginary nanosubmarine that would be constantly jostled around because the fluid molecules might be almost as big as it is.

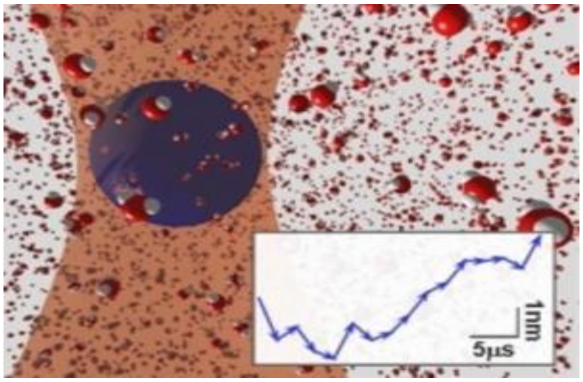


Fig. 1. 5 Brownian motion of small particles

- **Size dependent Properties: -** Size-dependent properties are the reason that nanoscale objects have the potential to significantly impact both science and industry.

- **Optical (e.g. color, transparency):-** The color of a material can also be size dependent. The appearance of color is caused by the partial absorption of light by electrons in that material; the unabsorbed part of the light remains visible. On most smooth metal surfaces, light is entirely reflected by the very high density of electrons; this is why the surfaces of slabs of metal have mirror-like appearance. In contrast, small particles absorb some of the light, leading to the appearance of color. This property depends on size [12]. For example, gold exhibits a different color depending on its particle size. Bulk gold appears yellow in color but nanosized gold appears red in color. The particles are so small that electrons are not free to move about as in bulk gold. Because this movement is restricted, the particles react differently with light [13].

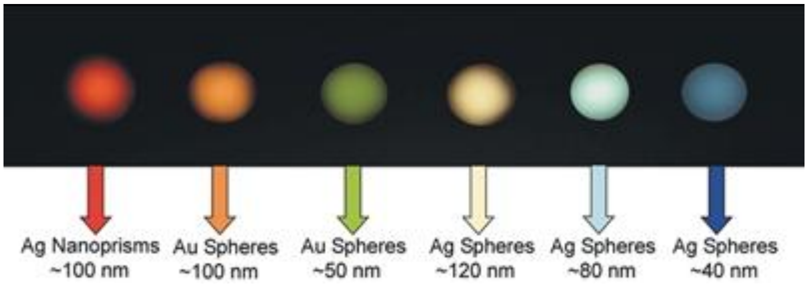


Fig. 1.6 Different nanosized particles of gold and silver have different colors.

- **Electrical (e.g. conductivity):-** At the nanoscale, electrical properties are not necessarily the same as they are on the macroscale. Materials that are conductors on the macroscale may lose their conductivity at the nanoscale and vice versa. For instance, when an insulator becomes thin enough, it can be rendered conductive through a process called quantum tunneling, a non-classical effect that is generally only observed at the nanoscale or smaller [14].

  Carbon in the form of graphite (like pencil lead) is soft and malleable; at the nano-scale carbon can be stronger than steel and is six times lighter. Nanotubes are long, thin cylinders of carbon. They are 100 times stronger than steel, very flexible, and have unique electrical properties. Their electrical properties change with diameter and number of walls. They can be either conducting or semi-conducting in their electrical behavior [15].

- **Physical (e.g. hardness, melting point):-** One of the unique properties of nanoparticles is that they have lower melting temperatures than their bulk material counterparts. As surface particles have fewer neighbours therefore less heat is required for their melting. That means that surface particles have lower melting point as compared to bulk particles which have more neighbours. Since at nanoscale surface area increases therefore nanoparticles have lower melting points.

  This melting point depression is used to define the nanoscale region as 1-100nm. Between the values of 1nm and 100nm, the change in melting temperature becomes readily noticeable. Above 100nm, the temperature change remains relatively close to zero. Below 1nm, melting point has no physical meaning as these sizes are governed by subatomic and single atom phenomenon [16].

- **Chemical (e.g. reactivity, reaction rates):-** Chemical reactions involve the atoms that lie at the surface of a material, thus chemical properties are dependent on surface properties. Since surface area at nanoscale is large therefore nanoparticles have enhanced reaction rates. Therefore nanoparticles are used as reaction catalysts.

  On the macroscale, gold is considered to be much less catalytically active than other transition metals. However, nanoscale particles of gold that are less than 8 nm in diameter can act as catalysts to enhance the rate of some chemical reactions. One possible application for these particles is in the catalytic converter, where harmful pollutants produced by automobiles such as carbon monoxide, react to form carbon dioxide and water. Automobiles generate most of their pollution within the first five minutes after starting up. Therefore, at the time the majority of the harmful pollutants are generated, the catalytic converter is ineffective due to the low temperature of the exhaust. The use of nanoscale gold particles for this application may help significantly reduce automobile-related air pollution since gold particles catalyze the reaction even at sub-zero temperatures [17].

1.1.7 Methods of synthesis:-

1) Top-down approach: - Top down approach refers to slicing or successive cutting of a bulk material to get nano sized particle. This approach has following processes:-
   - Ball milling
   - Photolithography
   - Etching
   - Sputtering

2) <u>Bottom-up approach: -</u> Bottom up approach refers to the build up of a material from the bottom: atom by atom, molecule by molecule or cluster by cluster. This approach has following processes:-

- Chemical precipitation
- Sol-gel
- Solvothermal
- Hydrothermal

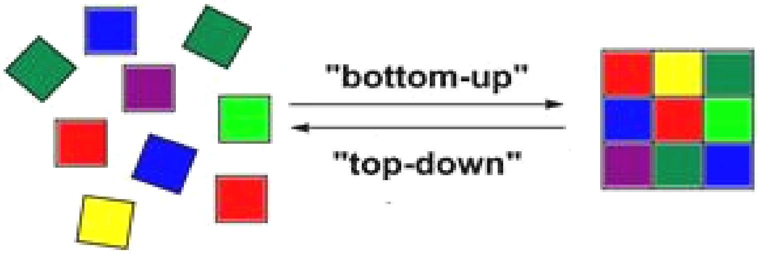


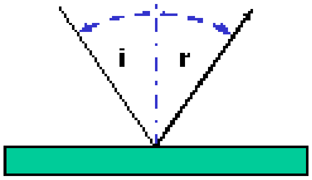
Fig. 1.7 Bottom up and Top down technique.

1.2 Reflectance:-

1.2.1 Introduction to Reflectance:-

The phenomenon by which a ray of light changes the direction of propagation when it strikes a boundary between different media is described as the reflection of light. Or in simpler words reflection is the bouncing of light from a smooth surface [18].

The law of reflection says that when a ray of light hits a surface, it bounces in a certain way, like a tennis ball thrown against a wall. The incoming angle, called the angle of incidence, is always equal to the angle leaving the surface, or the angle of reflection [19].



Law of Reflection

Reflectivity is the fraction of incident radiation reflected by a surface. In general it must be treated as a directional property that is a function of the reflected direction, the incident direction, and the incident wavelength. Reflectivity measures the fractional amplitude of the reflected electromagnetic field, while reflectance refers to the fraction of incident electromagnetic power that is reflected at an interface. The reflectance is thus the square of the magnitude of the reflectivity. The reflectivity can be expressed as a complex number as determined by the Fresnel Equations for a single layer, whereas the reflectance is always a positive real number.

$$R = \left|\frac{E_r}{E_i}\right|^2 = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2 .$$

In certain fields, reflectivity is distinguished from reflectance by the fact that reflectivity is a value that applies to thick reflecting objects. When reflection occurs from thin layers of material, internal reflection effects can cause the reflectance to vary with surface thickness. Reflectivity is the limit value of reflectance as the surface becomes thick. The reflectance spectrum or spectral reflectance curve is the plot of the reflectivity as a function of wavelength [20].

Rayleigh scattering is the elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength of the light, which may be individual atoms or molecules. The size of a scattering particle (r) and wavelength of light (λ) are related by ratio x:-

$$x = \frac{2\pi r}{\lambda}.$$

Rayleigh scattering can be defined as scattering in the small size parameter regime $x \ll 1$.

According to Rayleigh the intensity of the scattered light varies as the sixth power of the particle size and varies inversely with the fourth power of the wavelength i.e. [21]

$$I \propto 1/r^6 \quad \text{and} \quad I \propto 1/\lambda^4$$

1.2.2 Types of reflection:-

There are two types of reflection.

Regular Reflection or Specular Reflection

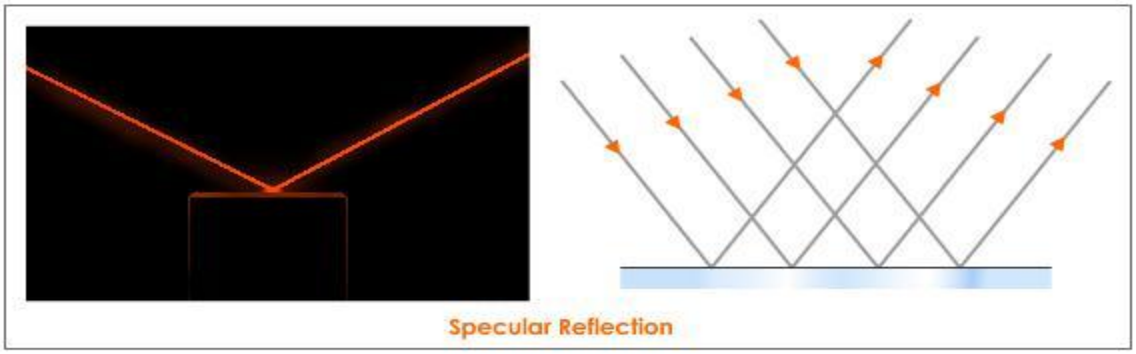


Fig. 1.8 Specular reflection

Specular or regular reflection is the perfect, mirror-like reflection of light. In this type of reflection the reflected rays are also parallel to each other. Reflection in a mirror, a water surface and highly polished floors, are examples of regular reflections.

Irregular Reflection or Diffused Reflection

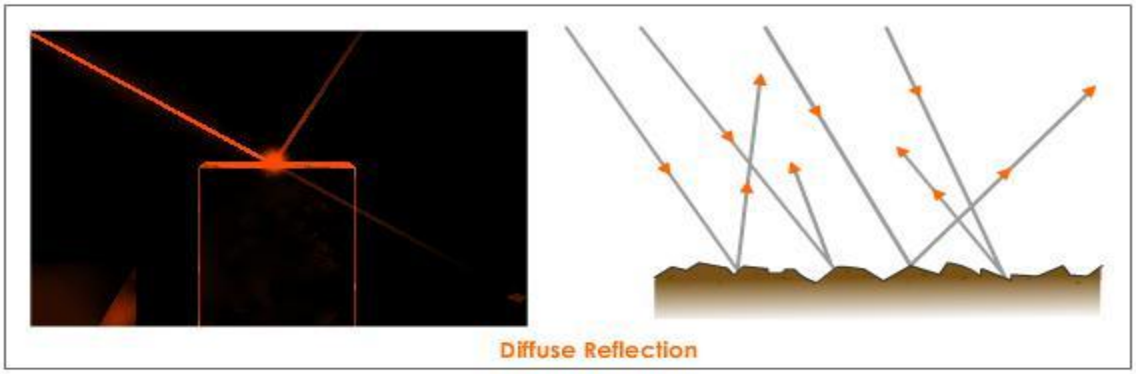


Fig. 1.9 Diffuse reflectance

Irregular reflection or diffused reflection takes place when a ray of light is incident on a wall or wood, which is not smooth or polished. In this case, the different portions of the surface reflect the incident light in different directions. In such cases no definite image is formed, but the surface becomes visible. It is commonly known as scattering of light. Thus diffused reflection makes non-luminous objects visible.

Not all light, which hits an object, is reflected. Some of the incident light is absorbed. The brightness of an object depends on the intensity of the incident light and also on the reflectivity of the object. If a surface allows the entire incident light to undergo regular reflection then it will become invisible [22].

1.2.3 Reflective coating:-

Reflective coatings are used in luminaries, search and spot lights, reflective panels, integrating sphere, photomultiplier tubes, interior walls and simply to protect the surface and also to give a color to the surface it is applied. Coating is composed of pigments, binder, solvent and other additives.

Pigments are granular solids added into the coating to provide basically color and toughness. Some coatingss may also contain dyes in combination with pigments. In addition to giving color to coatingss, pigments are also used to color the glass. Natural pigments include clays, calcium carbonate, mica, silicas and talks while synthetic pigments are usually engineered molecules.

The **binder** is the most crucial component of coating which forms the actual film. However, with the new technological developments today it is possible to find also binder-free coatings. The binder imparts adhesion, binds the pigments together and influences durability, flexibility, toughness and gloss potential of the coating. Binders include synthetic or natural resins i.e. acrylics, polyurethanes, melamine resins, epoxy or oils. So-called water based coatimgs include a water based dispersion of sub-micrometer sized polymer particles.

Solvents are used to control the thickness of the coating (to decrease the viscosity of the coating so that it can be easily brushed) and also to facilitate drying of the coating. Solvent evaporates during the course of drying releasing volatile organic compounds.

Nanotechnology impact on reflective coating:-

Various additives could be added to reflective coating to have significant impacts on the coating. Additives can modify surface tension, improve flow properties and the finished appearance, increase wet edge, etc. Nanomaterials are used as additives like fillers, pigments and etc. Usually nano additives / nanoparticles are embedded and fixed in organic polymer.

Nanometals or nanoceramic particles are added to the coating composition to change the final properties of the coating. Most common nanoparticles used are: TiO_2, ZnO, ZnS, Al_2O_3, fumed silica and ZrO_2. These materials are used in reflective coatings because they have high refractive index and wide band gap.

Rheology, settling, surface energy, corrosion resistance and mechanical properties of coating can be improved via addition of nanoparticles. By addition of these nanoparticles coating gets scratch-proof, easy cleaning, air purifying, UV resistant, water repellance, flame retardancy and anti-bacterial feature. Also nanoenhanced coatings dry faster than their normal counterparts without releasing any volatile organic compounds (VOCs) that impose health risks. There are also nanoenhanced coatings that improve the thermal insulation of buildings when applied to roofs, walls and floors.

Nanoenhanced coatings are produced the same way as normal coatings. Since nanoparticles are handled at the production site, more powerful ventilation systems need to be installed to ensure health and safety of workers [23].

Chapter 2

Materials and characterization

2.1 Materials properties:-

2.1.1 Properties of ZnS:-

Zinc sulfide is a chemical compound with the formula ZnS. Zinc sulfide is a white- to yellow-colored powder or crystal. It is typically encountered in the more stable cubic form, known also as zinc blende or sphalerite. The hexagonal form is also known both as a synthetic material and as the mineral wurtzite. Both sphalerite and wurtzite are wide-band gap semiconductors. The cubic form has a band gap of 3.54 eV at 300 K whereas the hexagonal form has a band gap of 3.91 eV. Refractive index of zinc blende is 2.369 eV and that of wurtzite is 2.356 eV .The transition from the sphalerite form to the wurtzite form occurs at around 1020 ºC.

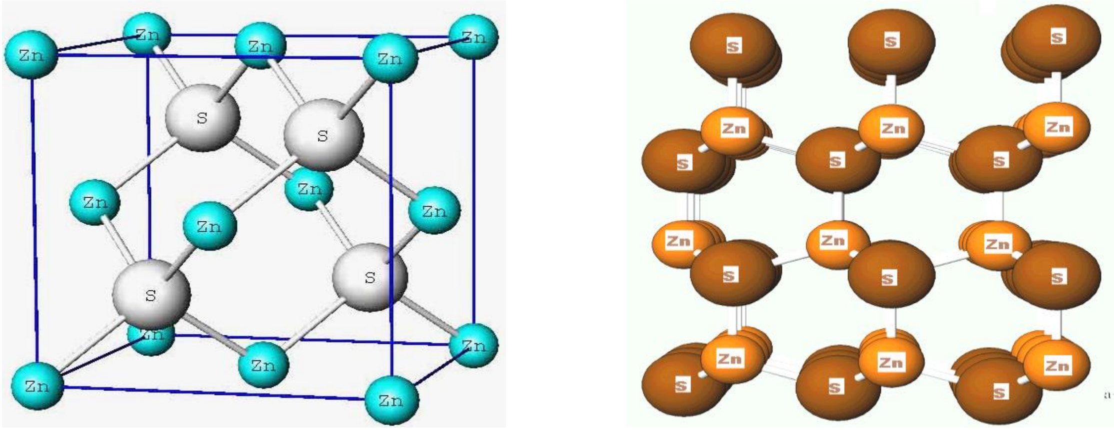


Fig. 2.1 Cubic zinc blende (sphalerite) and Hexagonal wurtzite structures

ZnS is used for a variety of applications such as optical coatings, photoconductors, optic modulators, electro-optic modulators, flat panel displays, electroluminescent devices, sensors, lasers and also have been applied in photo catalysis, infrared window, pigments and nonlinear optical devices [24].

2.1.2 Properties of Ni:-

ZnS can be doped with Ni. Ni has atomic number 28. Density of Ni is 8.9 g.cm^{-3} at 20°C. Melting and boiling point of Ni is 1453 °C and 2913 °C. Nickel is silvery-white, hard, malleable, and ductile metal. It is of the iron group and it takes on a high polish. It is a fairly good conductor of heat and electricity. In its familiar compounds nickel is bivalent, although it assumes other valences. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen. This metal has good mechanical properties and excellent resistance to many corrosive environments. Pure nickel has high electrical conductivity, a high Curie temperature and good magnetostrictive properties [25].

2.2 Characterization techniques: - Nanoparticles are characterized by following techniques in general:-

2.2.1 XRD: - X-ray crystallography is a standard technique for solving crystal structures. Its basic theory was developed soon after x-rays were first discovered more than a century ago [26]. It is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

Basic Principle:- In 1912, Max von Laue, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). Diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material [27].

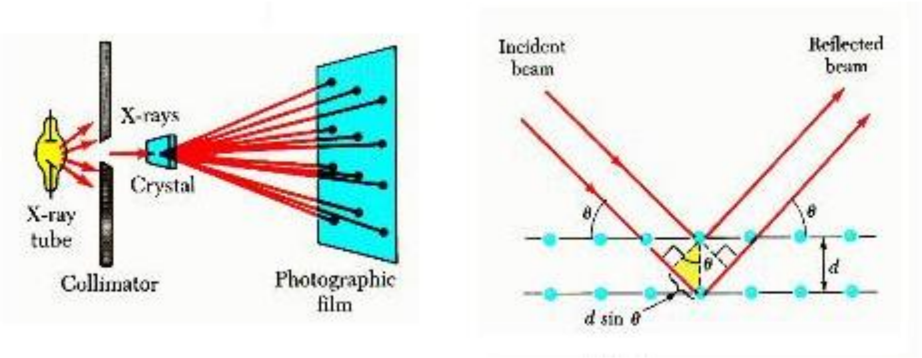


Fig. 2.2 Interaction of X-rays with a crystal produces diffraction pattern on a photographic film and Bragg’s diffraction

Data analysis [28]:-The diffraction pattern, that includes position (angles) and intensities of the diffracted beam, provides following information about the sample.

- Angles are used to calculate the interplanar atomic spacings (d-spacings). These d-spacings (d) and intensity (I) information are used to identify the type of material by comparing them with patterns in the International Powder Diffraction File (PDF), complied by the Joint Committee for Powder Diffraction Standards (JCPDS).

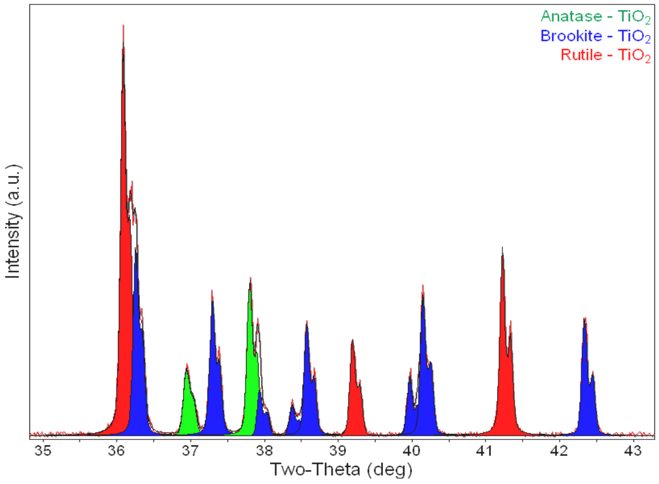


Fig. 2.3 Diffraction pattern for TiO_2

- The space between diffracting planes of atoms determines peak position ($\lambda=2d\sin\theta$).

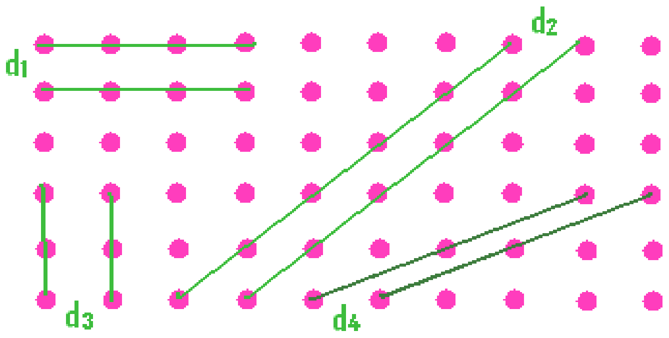


Fig. 2.4 Different planes in a crystal have different spacing

- The peak intensity is determined by atoms in the diffracting plane.

- Width of the diffracted peaks is used to determine crystallite size using Scherrer's equation.

$$t = (.9\lambda)/ (B\cos\Theta_B)$$

Where B is Full Width at Half Maximum (FWHM) and Θ_B is Bragg's angle.

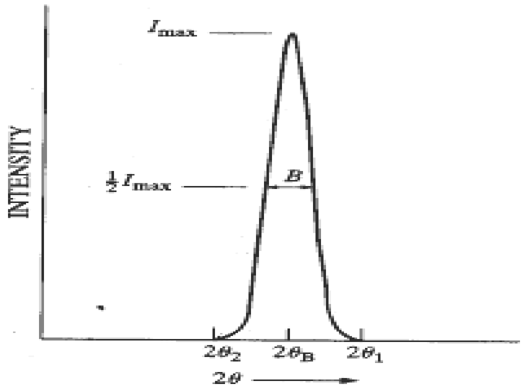


Fig. 2.5 FWHM and value of Θ_B from peak helps in calculating crystallite size

2.2.2 TEM: - The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light [29].

The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. TEM is capable of imaging at significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument to be able to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution and semiconductor research [30].

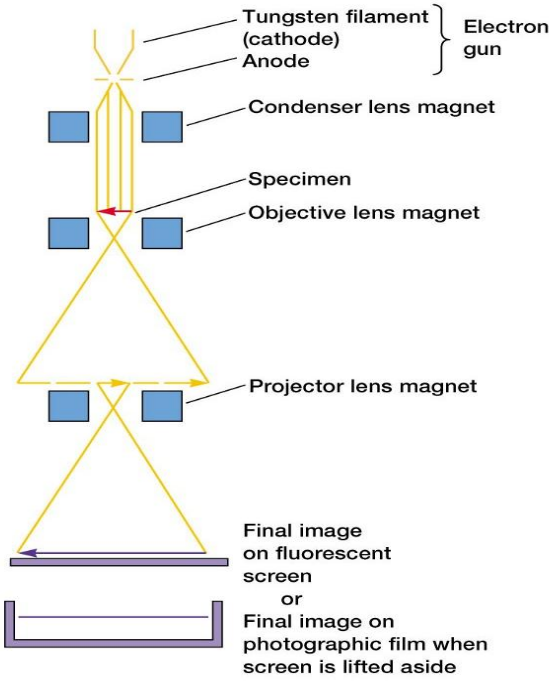


Fig. 2.6 TEM apparatus

Imaging modes: - TEM has two main imaging modes.

- In bright field imaging an aperture is placed in the back focal plane of the objective lens which allows only the direct beam to pass [31].

- In dark field imaging the direct beam is blocked by the aperture while one or more diffracted beams are allowed to pass the objective aperture [32].

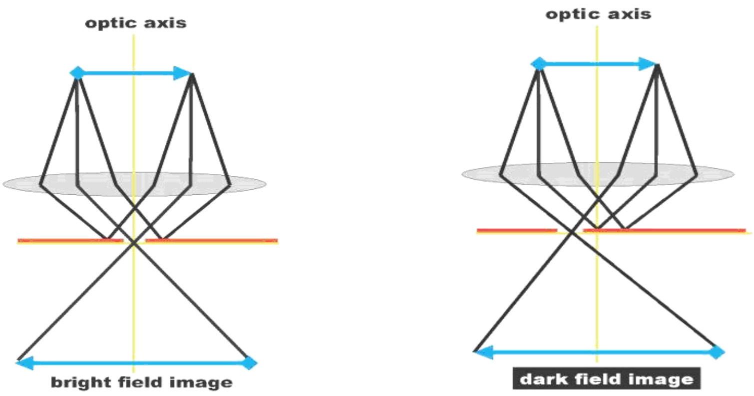


Fig. 2.7 Bright field imaging and dark field imaging

Data analysis [33]:-

Morphology: - TEM pattern gives the size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters.

Crystallographic Information: - It gives the arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter.

Compositional Information: - It tells about the elements and compounds of which the sample is composed of and their relative ratios, in areas a few nanometers in diameter.

2.2.3 UV-visible Spectroscopy**: -** Primarily used for quantitative analysis of known compounds, UV-Vis is one of the most popular techniques in the pharmaceutical, foods and paints Industries, as well as water laboratories [34]. The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $\mathbf{I_0}$. The intensity of the sample beam is defined as **I**. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm [35].

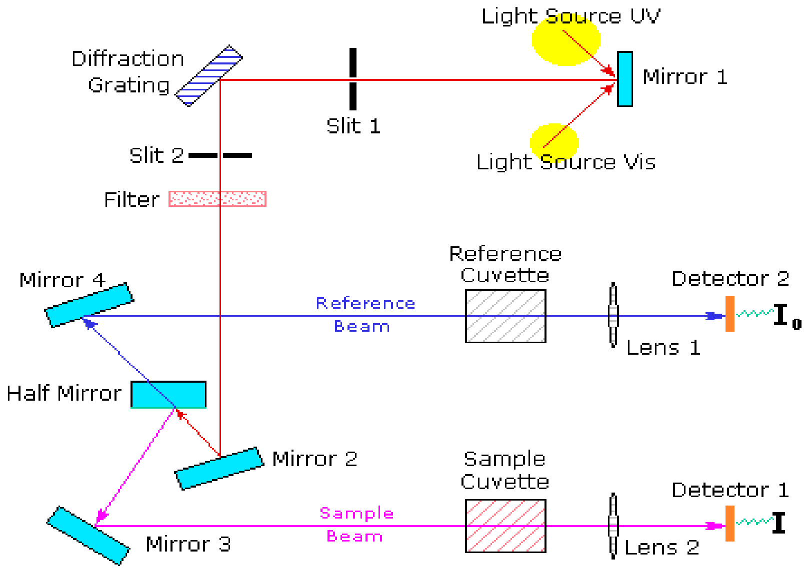


Fig. 2.8 Functioning of UV-Vis technique

Integrating sphere and its use: - An integration sphere is a spherical cavity, exhibiting Lambertian reflectance, which diffuses light in such a way that light reflected from the wall at any point would be distributed perfectly evenly over the surface of the sphere. Spatial integration is achieved upon a single reflection, and the radiance of the indirectly illuminated sphere wall would be both uniform and proportional to the total reflected flux. The integration sphere allows the detector to collect and spatially integrate the total radiant flux reflected diffusely from the sample [36].

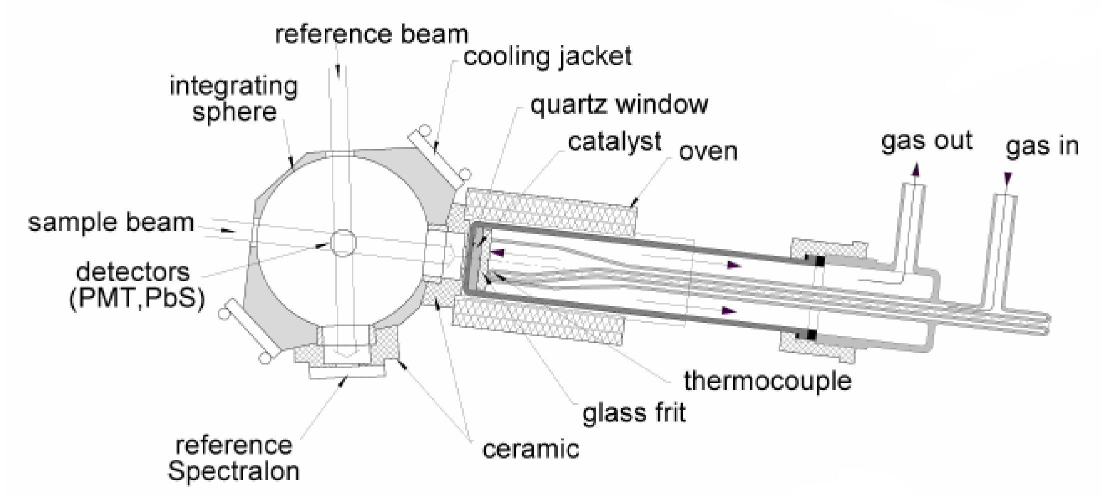


Fig. 2.9 Integrating sphere is used to see diffused reflectance of a material

Data analysis:-

Transmittance: $T = P/P_0$

Absorbance: $A = -\log 10\ T = \log 10\ P_0/P$

The Beer-Lambert Law: $A = ebc$

Where the absorbance A has no units, since $A = \log 10\ P_0 / P$

P_0 is the initial radiant power

P is the radiant power after light passes through sample

e is the molar absorbtivity with units of L mol^{-1} cm^{-1}

b is the path length of the sample in cm

c is the concentration of the compound in solution, expressed in mol L^{-1} [37].

The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the value of the optical band gap. The relation between the absorption coefficient (α) and the incident photon energy (hν) can be written as

$$(\alpha h\nu) = A\,(h\nu - Eg)^n$$

Where, A is a constant, Eg is the band gap of the material and exponent n depends on the type of transition.

The value of optical band gap is calculated by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs. (hν) graph to hν axis [38].

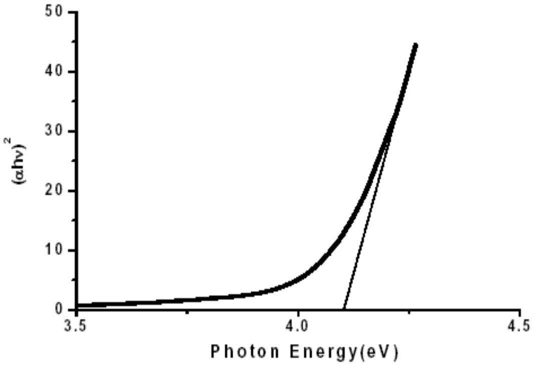


Fig. 2.10 Graph for ZnS nanoparticles

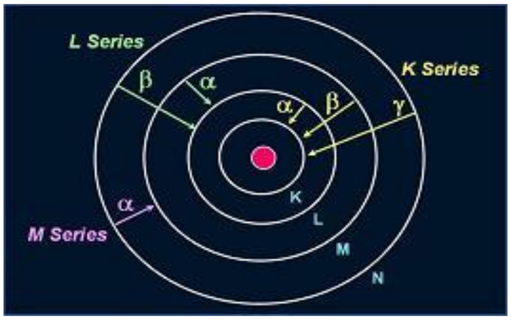
Kubelka-Munk Theory is used to define the absorption and scattering components of the spectrum. The Kubelka-Munk function is used to correct the diffuse reflectance spectrum to an absorption profile.

$$F(R) = \frac{(1-R)^2}{2R}$$

The application of Kubelka-Munk theory to the determination of the absorption profiles of diffusely reflecting materials relies on the fact that the Kubelka-Munk scattering coefficient is far less wavelength dependent than the absorption coefficient [39].

2.2.4 EDX spectroscopy: -

EDX Analysis stands for Energy Dispersive X-ray analysis. Energy dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit 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 each other.



To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. 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 while creating an electron hole where the electron was. An electron from an outer, 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 [40].

Data analysis:-The EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks are unique to an atom, therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. So EDX tells about the elemental composition [41].

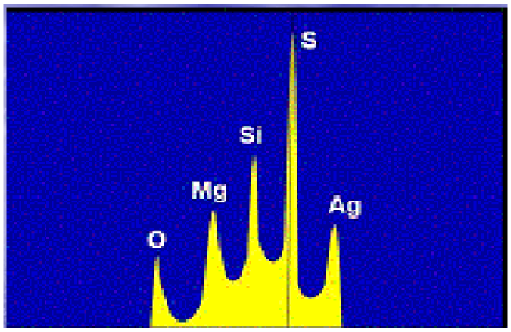


Fig. 2.11 An example of EDX spectrum

2.2.6 <u>Photoluminescence spectroscopy</u>**: -** Photoluminescence (PL) spectroscopy is a contact less, nondestructive method of probing the electronic structure of materials.

Typically, a laser beam impinges a sample, where it is absorbed. The excess energy brought to the material can be dissipated through the emission of light, or luminescence. As the excitation of the sample is performed by light, this luminescence is called "photoluminescence" [42].

Types of photoluminescence:-

There are two types of photoluminescence**;** fluorescence and phosphorescence**.**

1. Fluorescence is the emission of electromagnetic radiation light by a substance that has absorbed radiation of a different wavelength. Fluorescence arises from the decay of the excited single state S_1 to the ground state S_0. In most cases, absorption of light of a certain wavelength induces the emission of light with a longer wavelength (and lower energy). However, under conditions in which intense radiation is being absorbed, it is possible for one electron to absorb two photons (multiple photon absorption), which can lead to the emission of radiation having a smaller wavelength than the excitation source. The energy difference between the absorbed and emitted photons is due to thermal losses. Dissipation of vibrational energy occurs on a much greater time scale than fluorescent emission. The most striking examples of this phenomenon occur when the absorbed photon is in the ultraviolet region of the spectrum, and is thus invisible, and the emitted light is in the visible region [43].

2. Phosphorescence is a specific type of photoluminescence related to fluorescence. Unlike fluorescence, a phosphorescent material does not immediately re-emit the radiation it absorbs. The slower time scales of the re-emission are associated with "forbidden" energy state transitions in quantum mechanics. As these transitions occur less often in certain materials, absorbed radiation may be re-emitted at a lower intensity for up to several hours [44]. Phosphorescence arises from the decay of the excited triplet state T_1 to the ground state S_0. Phosphorescence is strictly forbidden by quantum mechanics since it involves a transition between pure states of different spin multiplicity, however, this forbidden ness can be relaxed by interactions between the magnetic dipoles generated by the spin of the electron and the orbital motion of the electron. These spin-orbit interactions lead to coupling of the singlet and triplet states, giving some singlet character to the triplet state, and thus to a small, but finite, transition probability, between T_1 and S_0 [45].

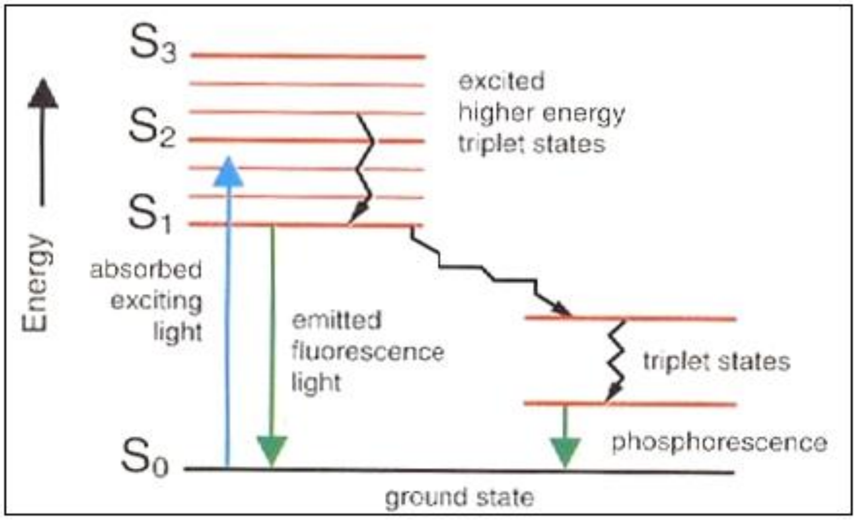


Fig. 2.12 Origin of fluorescence and phosphorescence

Experimental Set Up: - The basic elements of a PL spectroscopy set-up are [46]:-

- An optical source
- Collection lenses
- A spectrometer
- A detector

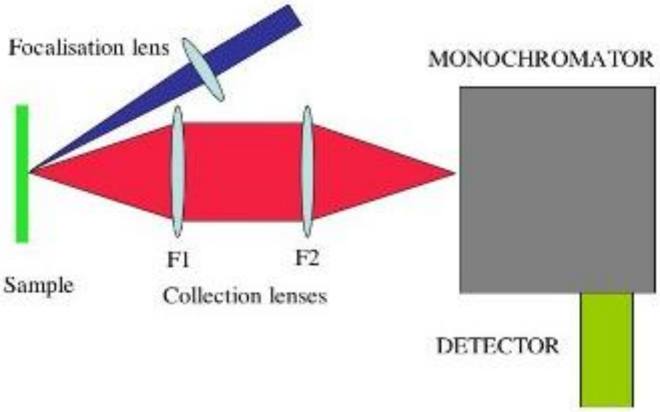
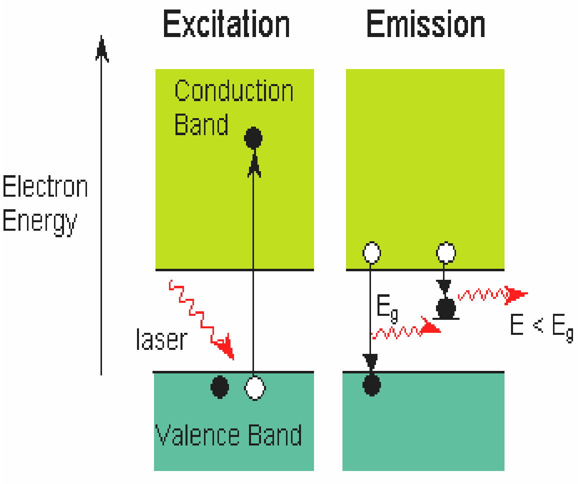


Fig. 2.13 Experimental set up for PL spectroscopy

Theory:-

The absorption of light causes the electrons of the atoms of the absorbing material to become excited and jump from the inner orbits of the atoms to the outer orbits. When the electrons fall back to their original state, photons of light are emitted. The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state.



Data output:-

Data output of PL spectroscopy is a graph with wavelength on x-axis and photoluminescence intensity on y-axis.

Advantages:-

1. Band Gap Determination: - The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the band gap. Band gap determination is particularly useful when working with new compound semiconductors.

2. Impurity Levels and Defect Detection: - Radiative transitions in semiconductors also involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration.

3. Recombination Mechanisms: - The return to equilibrium, also known as "recombination," can involve both radiative and nonradiative processes. The amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. Analysis of photoluminescence helps to understand the underlying physics of the recombination mechanism.

4. Material Quality: - In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination [47].

2.3 Literature review:-

Synthesis and characterization of ZnS nanoparticles has been carried out by many researchers. B. S. R. Devi et al. synthesized ZnS nanoparticles by chemical co precipitation method. These particles are characterized by XRD, FTIR, UV-VIS and EDAX spectroscopy. XRD showed that reaction temperature is one of the parameters to control particle size [48]. K. S. Rathore et al. prepared the different sizes of ZnS nanoparticles by chemical method using zinc chloride and thiourea as precursors. Particles are characterized by XRD and UV-VIS spectroscopy which showed that particle size can be controlled by molar concentration of reactant solution. Results show that with increasing molar concentration of reactant solution in case of ZnS, the particle size decreases [49]. T. T. Q. Hoa et al. prepared ZnS nanoparticles by hydrothermal method. Particles are characterized by XRD, TEM and UV-VIS spectroscopy techniques. Characterization shows that particle size and band gap can be controlled by Zn^{2+}:S^{2-} molar ratio. With increasing molar ratio, particle size decreases and band gap increases [50]. Li Zhang et al. synthesized the ZnS nanoparticles by hydrothermal method. XRD shows that short reaction time is favorable to cubic phase ZnS formation, while long reaction time is suitable for the formation of hexagonal phase ZnS. So the phase of particles can be turned by controlling the reaction times. Luminescence spectra show that the luminescence intensity of the particles is affected by the reaction time and temperature. Luminescence intensity increases with increasing reaction time and decreases with increasing temperature [51]. In 1997, Stanic et al. synthesized the nanosized ZnS particles by sol gel method. Formation of ZnS was confirmed by X-ray diffraction (XRD) and IR absorption spectra [52].

P. H. Borse et al. prepared the doped ZnS nanoparticles by a chemical method. Doping is done with Ni and Fe. XRD patterns are observed for doped and undoped particles. Luminescence spectra show the quenching in luminescence intensity on doping with nickel and iron [53]. P. Yang et al. synthesize the nickel doped ZnS nanoparticles by co precipitation method. Particles are characterized by XRD and UV-VIS spectroscopy [54]. P. Verma et al. reported the synthesis of Mn doped ZnS nanoparticles. Particles are characterized by XRD, TEM, FTIR and UV-VIS spectroscopy [55]. L. Sun et al. synthesize the copper doped ZnS nanoparticles by a chemical method. Absorption and excitation spectra of particles are observed. Photoluminescence spectra show that the emission peaks and intensities change with the concentration of Cu+ dopant ions [56]. W. Q. Peng et al. synthesized the copper doped ZnS nanoparticles by a wet chemical method. Particles are characterized by XRD, HRTEM, UV-VIS and PL spectroscopy. UV- VIS spectra show that absorption peak shifts with the variation of doping concentration. Band gap is more as compared to that of bulk ZnS. Undoped ZnS showed two blue luminescence peaks in PL spectra but copper doped ZnS show a third peak of green luminescence [57]. P. V. B. Lakshmi et al. prepared the Mn doped ZnS nanoparticles. Particles are characterized by XRD, UV-VIS and PL spectroscopy. Optical studies show that nanosized ZnS has a band gap of 3.9 eV blue shifted from bulk. Photoacoustics and EPR studies are also done on doped ZnS. The EPR spectrum of ZnS: Mn shows a broad line which is the characteristic feature of the ferromagnetism [58].

Chapter 3

Synthesis

3.1 **Method of preparation**

3.1.1 Chemical precipitation

Precipitation is the formation of a solid in a solution during a chemical reaction. When the reaction occurs, the solid formed is called the precipitate, and the liquid remaining above the solid is called the supernate. Natural methods of precipitation include settling or sedimentation, where solid forms over a period of time due to ambient forces like gravity or centrifugation. During chemical reactions, precipitation may also occur particularly if an insoluble substance is introduced into a solution and the density happens to be greater (otherwise the precipitate would float or form a suspension). With soluble substances, precipitation is accelerated once the solution becomes supersaturated [59].

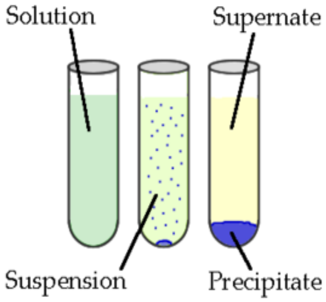


Fig. 3.1 Formation of precipitates

A common example is that of the mixing of two clear solutions: (1) silver nitrate ($AgNO_3$) and (2) sodium chloride (NaCl). The reaction is

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

The precipitates form because the solid (AgCl) is insoluble in water [60].

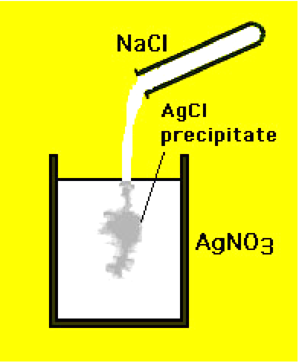


Fig. 3.2 Formation of AgCl precipitates

3.2 Synthesis of undoped and doped ZnS nanoparticles

In present work, undoped and nickel doped ZnS nanoparticles capped with thioglycerol were prepared by simple chemical precipitation method. The chemicals used for the synthesis are sodium sulphide (Na_2S), zinc acetate, nickel sulphate ($NiSO_4$) as doping agent and thioglycerol as capping agent.

3.2.1 Synthesis of undoped ZnS nanoparticles with different concentrations of zinc acetate and sodium sulphide

Five samples of undoped ZnS nanoparticles were prepared with following combinations of zinc acetate and sodium sulphide.

S.No.	Molar conc. of zinc acetate	Molar conc. of sodium sulphide
1.	1.0 M	0.2 M
2.	0.8 M	0.4 M
3.	0.6 M	0.6 M
4.	0.4 M	0.8 M
5.	0.2 M	1.0 M

Synthesis was done in following steps:-

1. Desired weight of zinc acetate and sodium sulphide was taken in 200 ml water and stirred for 45 min. These were required molar solutions of zinc acetate and sodium sulphide.
2. Molar solution of sodium sulphide was mixed drop wise to molar solution of zinc acetate and stirred for 30 min.
3. The white precipitates formed in above process were filtered and washed several times with distilled water and finally with ethanol.
4. Precipitates were dried in an oven at 70^0C for 24 hours and then crushed to fine powder and preserved in air tight containers.

Reflectance was checked for all samples and it comes out to be maximum for sample with same molar concentration of zinc acetate and sodium sulphide. Therefore different samples were prepared with same molar concentration of zinc acetate and sodium sulphide in order to see which concentration can be used in further work.

3.2.2 Synthesis of undoped ZnS nanoparticles with same molar concentration of zinc acetate and sodium sulphide

Six samples of undoped ZnS nanoparticles were prepared with following combinations of zinc acetate and sodium sulphide. Synthesis was done similarly as done for undoped ZnS nanoparticles with different combinations of zinc acetate and sodium sulphide.

S.No.	Molar conc. of zinc acetate	Molar conc. of sodium sulphide
1.	0.1 M	0.1 M
2.	0.3 M	0.3 M
3.	0.5 M	0.5 M
4.	0.7 M	0.7 M
5.	0.9M	0.9M
6.	1.1 M	1.1 M

Reflectance study of these samples shows that reflectance of sample with molar concentration 0.5 M is maximum; therefore this sample is used for further studies.

3.2.3 Synthesis of doped/capped ZnS nanoparticles

Four samples of ZnS doped with Ni and capped with thioglycerol were prepared with following combinations of zinc acetate, sodium sulphide and nickel sulphate:-

S.No.	Molar conc. of zinc acetate	Molar conc. of sodium sulphide	Molar conc. of nickel sulphate
1.	0.5 M	0.5 M	0.0003 M

2.	0.5M	0.5 M	0.0005 M
3.	0.5 M	0.5 M	0.1 M
4.	0.5 M	0.5 M	0.5 M

Synthesis was done in following steps:-

1. 0.5 M solutions of zinc acetate and sodium sulphide in 200 ml water were prepared. Stirring was done for 45 min.
2. Desired weight of nickel sulphate was taken in 50 ml water and stirred for 10 min. This was required doping agent.
3. 1 ml of thioglycerol was taken in 50 ml of 2- propanal and stirred for 10 min. to prepare required capping agent.
4. Prepared doping agent was mixed drop wise to 0.5 M zinc acetate solution and stirred for 30 min.
5. Capping agent prepared in step 3 was mixed drop wise to 0.5 m sodium sulphide and stirred for 30 min.
6. Solution prepared in step 4 was mixed drop wise to solution prepared in step 5 and stirred for 30 min.
7. The white precipitates formed in above process were filtered and washed several times with distilled water and finally with ethanol.
8. Precipitates were dried in an oven at 70^0C for 24 hours and then crushed to fine powder and preserved in air tight containers.

Chapter 4

Results and discussion

4.1 Structural analysis

4.1.1 X-Ray diffraction studies

XRD study is an efficient tool for analyzing the structural properties of the sample. Fig. 4.1 shows the x-ray diffraction pattern for ZnS nanoparticles with varying Zn : S molar concentration. Three prominent peaks corresponding to (111), (220), and (311) reflection planes of ZnS were observed respectively at 2θ of 29.04, 48.06, and 57.11. The diffraction peaks from (111), (220), and (311) planes have only appeared in the pattern and all other high-angle peaks have submerged in the background due to the large line broadening, which is attributed to nanosize of the particles. On comparing with the standard sample (JCPDS card No. 050566), the X-ray diffractogram and 2θ values of ZnS were found to be in fairly good agreement, thus confirming the zinc blende crystal structure. The broadening in the diffraction peaks might be due to the size effect, i.e., the crystallite size is in the nano-regime. These nanocrystals have lesser lattice planes compared to bulk, which contributes to the broadening of the peaks in the diffraction pattern. . It could also arise due to lack of sufficient energy needed by an atom to move to a proper site in forming the crystallite [61]. Width of peaks becomes larger as the particles become smaller [62].

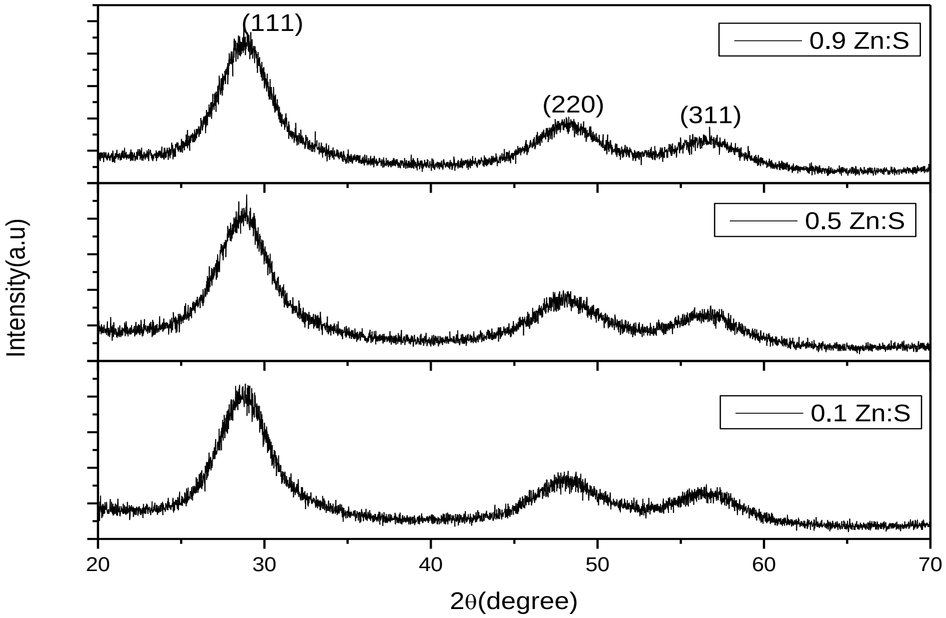


Fig. 4.1 X-ray diffraction patterns for ZnS nanoparticles with varying Zn: S ratio

Figure 4.2 shows the x-ray diffraction pattern for Ni doped ZnS nanoparticles with varying molar concentration of nickel sulphate ($NiSO_4$). Ni atoms were added to the host lattice of ZnS. Three types of nickel microstructures could in general be formed. Nickel atoms may substitutionally occupy Zn sites, nickel clusters or nickel sulphite (NiS) may be formed. No characteristic peaks of Ni have been observed that mean dopant does not affect the crystal structure. There is not much difference between peaks of the doped and the undoped samples in XRD pattern. From the results, it was assumed that, the added quantity of capping agent (thioglycerol) is enough to prevent the agglomeration of particles [63].

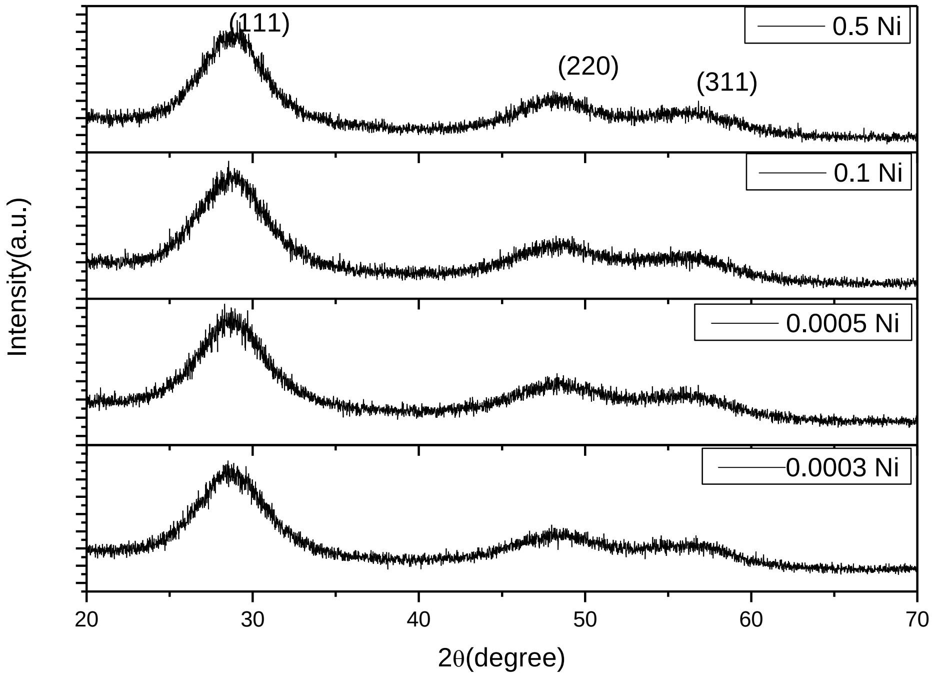


Fig. 4.2 X-ray diffraction pattern for Ni doped ZnS nanoparticles with varying molar concentration of nickel sulphate.

The crystallite size of undoped ZnS nanoparticles and that of doped ZnS nanoparticles doped with different concentrations of dopant is estimated from Debye Scherrer formula:-

$$D = 0.91\lambda / \beta\cos\Theta$$

D = crystallite size, λ = wavelength of CuKα (1.542 A^0), β = full width at half maxima (FWHM), Θ = Bragg's angle

Table for crystallite size of undoped ZnS nanoparticles with varying Zn: S ratio:-

S.No.	Sample	Zn:S ratio	Crystallite size
1.	Undoped ZnS	0.1:0.1	2.665nm
2.	Undoped ZnS	0.5:0.5	2.476nm
3.	Undoped ZnS	0.9:0.9	2.470nm

From table it can be concluded that crystallite size of undoped ZnS nanoparticles comes out in the range of 2 nm and crystallite size decreases as the Zn:S ratio increases. It is indicating that crystallite size decreases with increasing molar concentration.

Table for crystallite size of doped ZnS nanoparticles with varying molar concentration of nickel sulphate:-

S.No.	Sample	Zn:S ratio	Molar concentration of $NiSO_4$	Crystallite size
1.	Doped ZnS	0.5:0.5	0.0003M	2.679nm
2.	Doped ZnS	0.5:0.5	0.0005M	2.550nm
3.	Doped ZnS	0.5:0.5	0.1M	2.530nm
4.	Doped ZnS	0.5:0.5	0.5M	2.240nm

From table it can be concluded that crystallite size of doped ZnS nanoparticles comes out in the range of 2 nm and crystallite size decreases as the molar concentration of $NiSO_4$ increases. It is indicating that crystallite size decreases with increasing molar concentration of dopant.

4.1.2 TEM analysis

The study of surface morphology of ZnS : Ni NPs has been carried out by TEM. Figure 4.3 shows the TEM micrograph of sample. From the TEM micrograph, the diameter of ZnS nanoparticles is estimated to be 10-20 nm. The particles are monodispersed and nearly spherical but they are not uniform in shape. As compared to the XRD each nanoparticle consists of 5-10 crystallites [64].

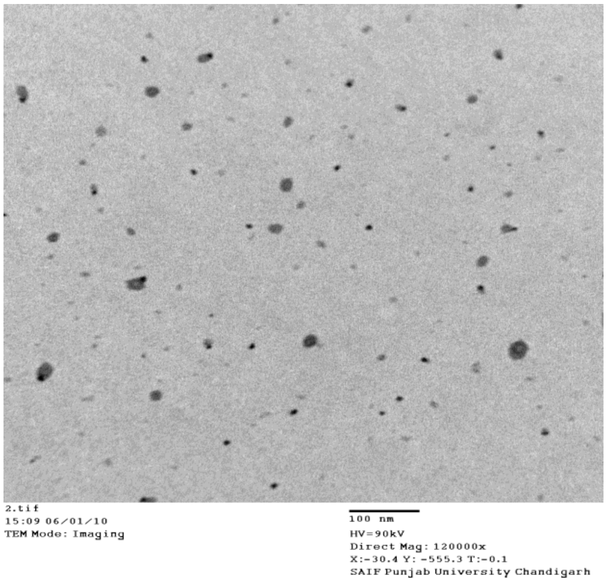


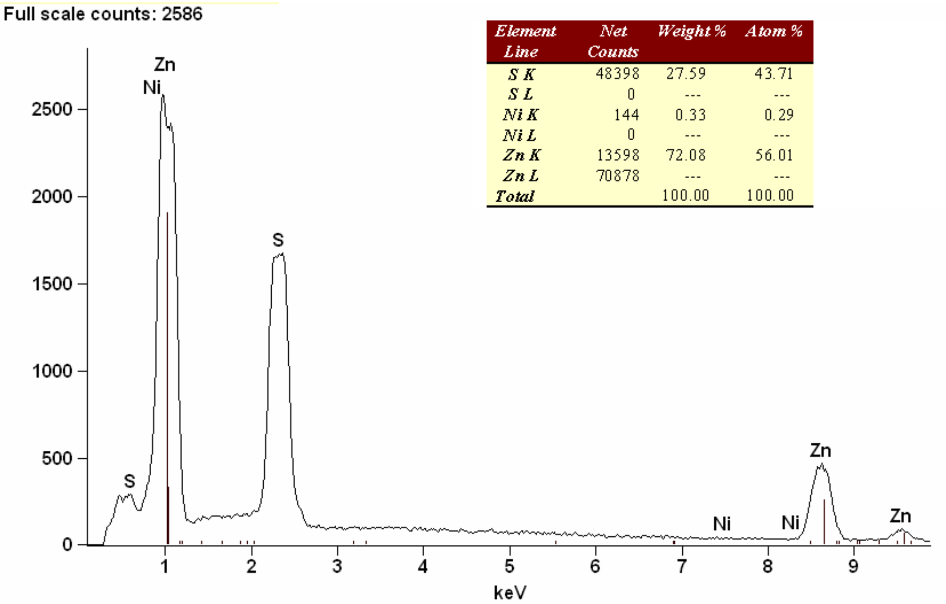
Fig. 4.3 TEM image of the Ni (0.1 M) doped ZnS nanoparticles

4.1.4 Energy Dispersive X-ray (EDX) Spectroscopy:-

EDX spectroscopy is an analytical tool to determine the composition of the sample. The composition of the ZnS : Ni nanoparticles were analyzed by EDX spectroscopy. Electron beam induced inner-shell ionization and subsequent emission of characteristic fluorescence are analyzed in order to obtain the composition. As shown in figure 4.4 and 4.5 Zn L fluorescence (Lα around 1 keV energy range), Zn K-fluorescence (Kα in the energy range 8-9 keV and Kβ in the energy range 9-10 keV), S K fluorescence (Kα in 49 the 2-3 keV energy range) and Ni K & L-fluorescence are observed. Figure 4.4 and 4.5 reveals that the Ni^{2+} ions may be incorporated in the Zn^{2+} lattice sites. We get the composition of our sample.

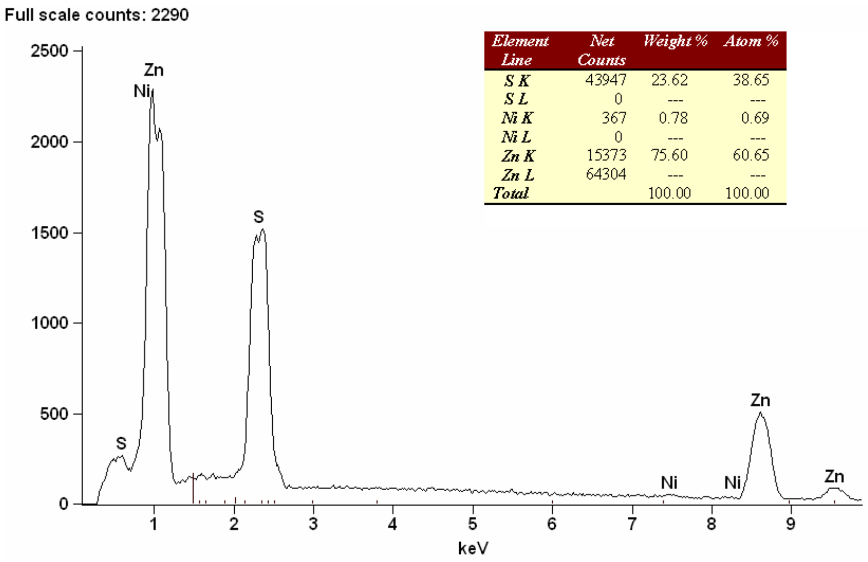
For sample ZnS:Ni containing 0.1 M $NiSO_4$, about 72.08% of Zn ion, about 27.59% of S ion and about 0.33% of Ni ion by weight are present in the sample. This shows that the incorporation of Ni is quite poor in the ZnS nanoparticles.

For sample ZnS:Ni containing 0.5 M $NiSO_4$, about 75.60% of Zn ion, about 23.62% of S ion and about 0.78% of Ni ion by weight are present in the sample [65].



Element Line	*Net Counts*	*Weight %*	*Atom %*
S K	48398	27.59	43.71
S L	0	---	---
Ni K	144	0.33	0.29
Ni L	0	---	---
Zn K	13598	72.08	56.01
Zn L	70878	---	---
Total		100.00	100.00

Fig. 4.4 EDX spectrum of the ZnS:Ni sample for 0.1M $NiSO_4$



Element Line	*Net Counts*	*Weight %*	*Atom %*
S K	43947	23.62	38.65
S L	0	---	---
Ni K	367	0.78	0.69
Ni L	0	---	---
Zn K	15373	75.60	60.65
Zn L	64304	---	---
Total		100.00	100.00

Fig. 4.5 EDX spectrum of the ZnS:Ni sample for 0.5M $NiSO_4$

4.2 Optical studies

4.2.1 Photoluminescence studies

Fig. 4.7 shows the photoluminescent spectra of doped and undoped ZnS nanocrystals. All the plots contain one peak centered at 430 nm. Appearance of a broad peak centered at 430 nm is attributed to the presence of sulphur vacancies in the lattice. The 420 – 430nm peak in ZnS has been classically termed as self activated luminescence and known to be due to recombination of carriers between sulphur vacancy (V_S) related donor and valence band [66].

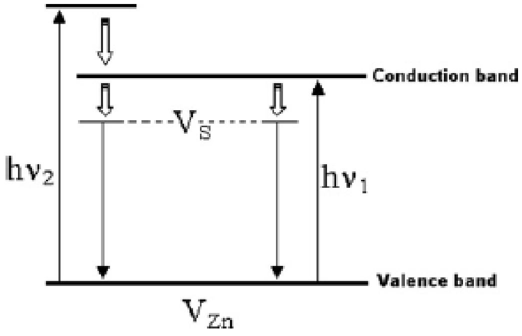


Fig. 4.6 Luminescence mechanism of ZnS nanoparticles V_{Zn} represents the acceptor level at zinc and V_S the sulfur vacancy donor level

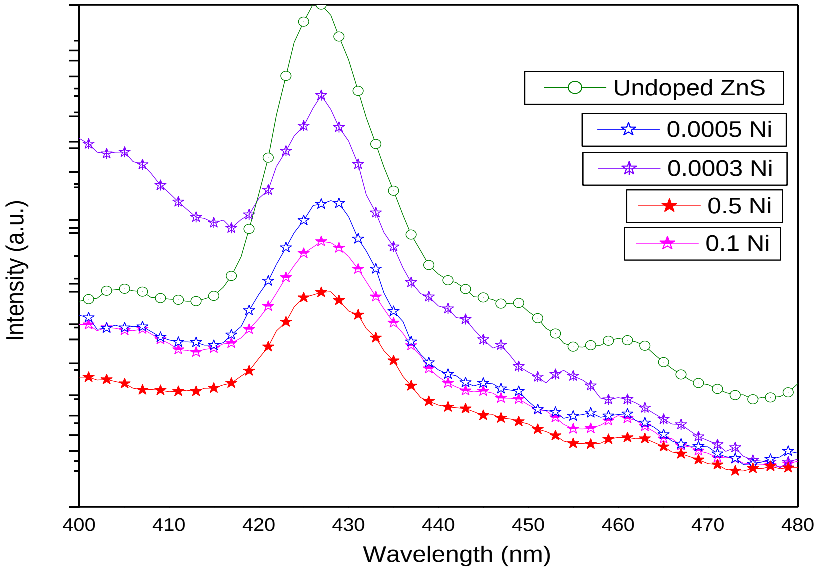


Fig. 4.7 Photoluminescent spectra of doped and undoped ZnS nanocrystals.

4.2.2 UV-Vis absorption studies:-

Undoped and Ni doped ZnS nanoparticles, finely dispersed in ethanol, have been used for the UV- visible absorption studies. Figure 4.8 shows the absorption spectra for undoped and doped ZnS nanoparticles. Band gap was calculated from absorption vs. wavelength graph by plotting $(\alpha h\nu)^2$ against hν and then extrapolating the straight portion of the curve on hν axis [67].

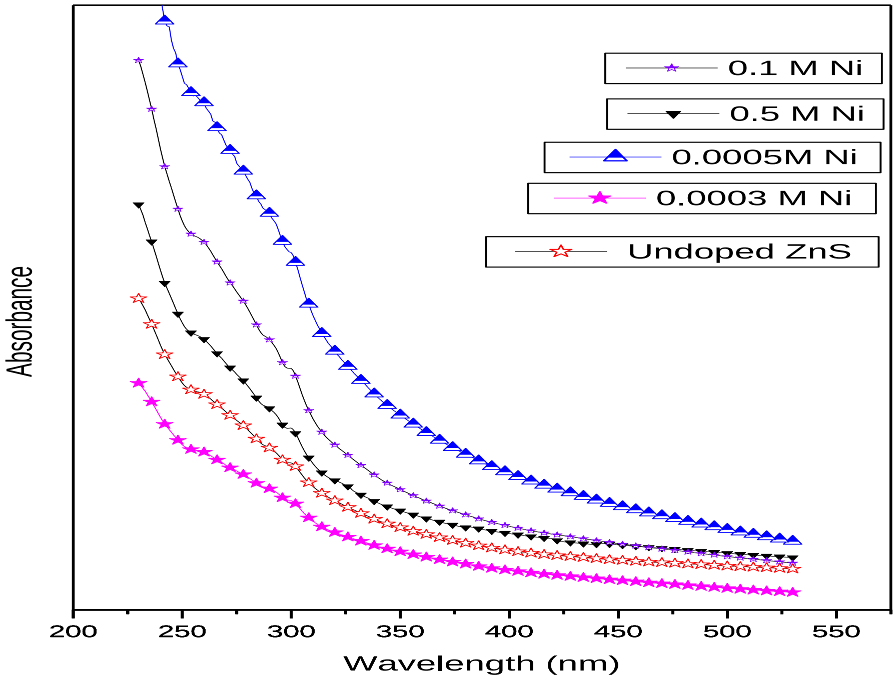


Fig. 4.8 Absorption spectra for undoped and doped ZnS nanoparticles

Table for band gap values of undoped and doped ZnS nanoparticles:-

S.No.	Sample	Zn:S	Dopant concentration	Band Gap
1.	Undoped ZnS	0.5:0.5	------------	3.90eV
2,	Doped ZnS	0.5:0.5	0.0003M Ni	4.0eV
3.	Doped ZnS	0.5:0.5	0.0005M Ni	4.10eV
4.	Doped ZnS	0.5:0.5	0.1M Ni	4.12eV
5.	Doped ZnS	0.5:0.5	0.5M Ni	4.2eV

Table shows that band gap increases as the molar concentration of dopant increases.

4.2.3 Reflectance studies:-

Figure 4.9 shows the diffuse reflectance spectra for undoped and doped/capped ZnS nanoparticles. Curve 4.9(a), (b), (c) and (d) shows the reflectance spectra of doped samples having diffuse reflectance 92-97%, 92-96%, 85-95% and 50-75% respectively for the visible region. From the spectra, with the increase in the dopant concentration there is decreases in the reflectance, this might be due to the absorption energy level introduced by dopant. Samples doped with 0.0003 M and 0.0005 M concentration of Ni show the higher reflectance as compared to undoped (curve 4(c)) sample. Ni is known as photoluminescence quencher and it replace the vacancy created by S^{2-} ion in the ZnS which is also observed in PL spectra, hence there is increase in the reflectance. With further increase in the doping concentration i.e. at 0.5 M (curve 4(d)), there is decrease in

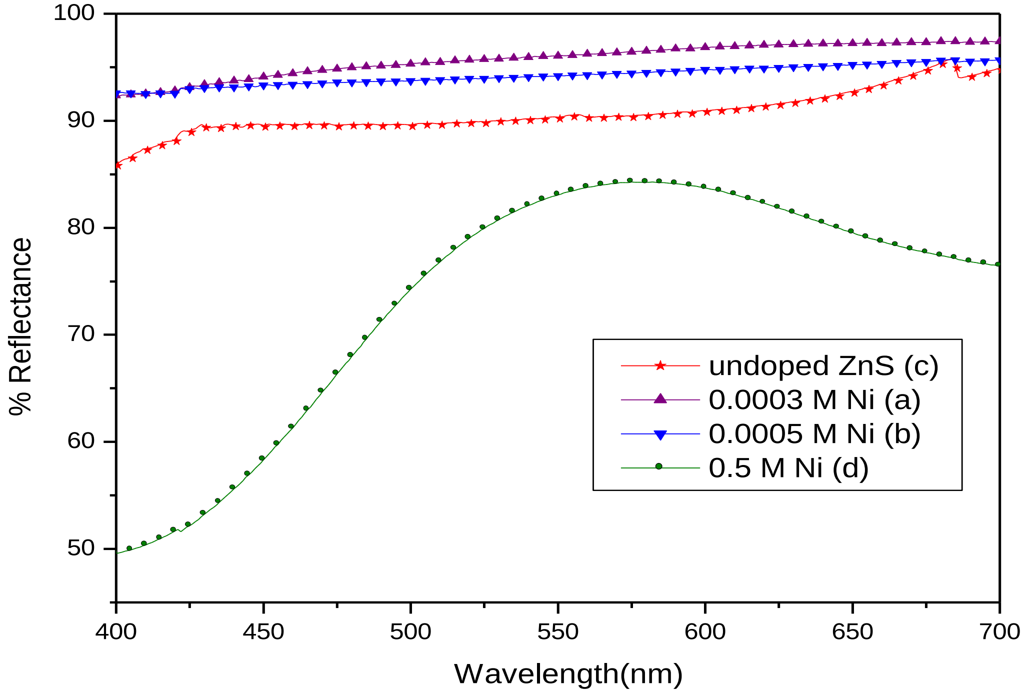


Fig. 4.9 Reflectance of Undoped and doped ZnS nanoparticles

the reflectance because Ni introduce new energy level in the band structure of ZnS [68]. It acts as electron trapping center which results into nonradiative recombination [69]. Therefore reflectance decreases as the molar concentration of dopant increases.

Chapter 5

Conclusions

5.1 Conclusions:-

The nanoparticles of ZnS Doped with different molar concentrations of Ni were successfully synthesized using well known chemical precipitation technique.

- These NPs were characterized structurally by XRD and found to have cubic crystal structure with the diffraction peaks as (111), (220), and (311). The crystallite sizes of the undoped and doped ZnS nanoparticles have been calculated using Debye Scherrer’s formula, which shows that crystallite size decreases as the Zn:S ratio increases and also size decreases as the molar concentration of dopant increases.

- Surface morphology of the NPs was studied by TEM. The NPs have been found to be nearly spherical in shape and possess average size of ~ 10 nm.

- The elemental analysis has been carried out by EDX. ZnS doped with 0.1 M Ni has atomic % of Zn, S and Ni respectively as 72.08, 27.59 and 0.33; and when ZnS is doped with 0.5 M Ni, atomic % of Zn, S and Ni has been found to be respectively 75.60, 23.62 and 0.78.

- The study of defects and color centre in ZnS:Ni was carried out by a flourospectrometer. The photoluminescent spectra of doped and undoped ZnS nanocrystals shows that all the plots contain one peak centered at 430 nm and appearance of this peak is attributed to the presence of sulphur vacancies.

- The optical band gap values for undoped and doped ZnS nanoparticles have been calculated from the absorbance versus energy plots using UV-Vis absorption spectra and it is found to vary from 3.9 eV to 4.2 eV. It shows that band gap of ZnS increases as the concentration of dopant increases.

- The diffuse reflectance spectrum was obtained using integrating sphere. Reflectance study for undoped and doped/capped ZnS nanoparticles shows that reflectance of ZnS nanoparticles, doped with 0.0003 M of Ni has been maximum.

Thus ZnS nanoparticles doped with 0.0003 M of Ni have been found to be extremely good as reflective pigment.

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