A STUDY OF Fe DOPING ON CORUNDUM NANOPARTICLES SYNTHESISED Via PRECIPITATION METHOD

Dissertation submitted to Department of physics, MES Asmabi College, P.Vemballur
(Affiliated to University of Calicut)

In partial fulfilment for the award of the degree of

MASTER OF SCIENCE
IN
PHYSICS

Submitted By,

KRISHNENDU.P.V
REG NO: AIAWMPH006

Under the esteemed supervision and guidance of:

Dr. SAFEERA.T.A
Assistant Professor, Dept.of Physics
MES Asmabi College, P.Vemballur

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Dr. SAFEERA.T.A
ASSISTANT PROFESSOR
MES ASMABI COLLEGE
P.VEMBALLUR

Department of Physics,

MES Asmabi College, P.Vemballur-680671

CERTIFICATE

This is to certify that the dissertation entitled " A study of Fe doping on Corundum nanoparticles synthesised via Precipitation method" is a bonafide record of work done by **KRISHNENDU.P.V (AIAWMPH006)** at MES Asmabi College, P. Vemballur under the guidance of **Dr. SAFEERA.T.A**, in partial fulfilment of the requirements for the award of Master of Science in Physics of Department of Physics, MES Asmabi College, Calicut University during the period of 2022-2024.

Head Of The Department

Dr. Ebitha Eqbal

Associate Professor

Dept.of Physics

MES Amabi College

P.Vemballur

A STUDY OF Fe DOPING ON CORUNDUM NANOPARTICLES SYNTHESISED Via PRECIPITATION METHOD

Submitted By,

KRISHNENDU.P.V
Reg.No.AIAWMPH006

This project presentation/viva voce held on ………………………… at MES Asmabi College, P.Vemballur , is evaluated and approved by,

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DECLARATION

I hereby declare that this submission, "**A Study Of Fe Doping On Corundum Nanoparticles Synthesised Via Precipitation Method**" is a record of my project work carried out under the guidance of Dr. Safeera. T.A, Assistant Professor, Department of Physics, MES Asmabi College, P.Vemabllur. I also declare that this project work has not been submitted previously for the award of any degree or diploma earlier. The findings in the report are based on the information collected by me and not copied from elsewhere.

P.Vemballur
17/07/2024

KRISHNENDU.P.V
Reg No: AIAWMPH006
M.Sc Physics
Dept.of Physics
MES Asmbai College

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KRISHNENDU.P.V
Reg No: AIAWMPH0

ABSTRACT

Nanotechnology, involving the manipulation of matter at the nanoscale, offers groundbreaking advancements across various fields. First introduced by Richard Feynman and coined by Norio Taniguchi, it includes both nanoscience and the practical application of nanoscale structures. Nanoparticles, ranging from 1 to 100 nanometers, exhibit unique properties due to increased surface area and quantum effects, driving innovations in healthcare, electronics, textiles, and more. These materials, classified by dimensions (0D, 1D, 2D, 3D), are crucial in addressing global challenges in energy, water, health, and technology, with over 800 nanotechnology-enhanced products on the market.

Nanoparticle synthesis involves top-down and bottom-up approaches. Top-down methods, like mechanical milling, electrospinning, and nanolithography, reduce bulk materials into nanoparticles. Bottom-up techniques, such as sol-gel synthesis, chemical vapor deposition, and pyrolysis, build nanoparticles atom-by-atom, molecule-by-molecule. Characterization techniques including X-ray diffraction, diffuse reflectance spectroscopy, photoluminescence, EDAX, and scanning electron microscopy (SEM) analyze nanoparticles' composition, structure, and properties.

Aluminium oxide (Al_2O_3) nanoparticles are porous nanomaterials with various crystalline phases, used widely in ceramics, catalysis, and biomedical applications due to their electrical insulation, high heat conductivity, and hardness. They are typically synthesized using methods like chemical precipitation, which involves mixing aluminium sulfate and sodium hydroxide to produce Al_2O_3. This method can also produce iron-doped aluminium oxide by adding iron chloride, resulting in nanoparticles with specific structural and optical properties analyzed through techniques like X-ray diffraction and scanning electron microscopy.

Aluminium oxide and iron-doped aluminium oxide nanoparticles were synthesized using the chemical precipitation method and characterized through various techniques. X-ray diffraction confirmed a trigonal structure with average crystallite sizes of 11.3 nm and 12.5 nm for pure and doped samples, respectively. SEM analysis revealed agglomerated circular structures, while EDAX confirmed the elemental composition. Photoluminescence spectra showed peaks at 335 nm and 385 nm, and diffuse reflectance studies indicated a bandgap energy reduction from 5.8 eV in pure Al2O3 to 3.26 eV in the doped sample.

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CHAPTER 1

1. INTRODUCTION

In the past few years nanotechnology has become the most important forefront in the fields of physics, chemistry, biology and engineering. It shows great promise for providing us in the near future with a lot of breakthroughs that will change the way of technological advances in a variety of applications. The ideas that gave rise to nanotechnology were initially talked about by the scientist Richard Feynman in 1959 in his talk ‘There is plenty of room at the bottom’. And the term “Nano-technology” was first used in 1974 by Norio Taniguchi. The prefix ‘nano’ in the term “nano-technology” means ‘a billionth’. It deals with different structures of matter having dimensions of order of a billionth of a meter. While the term nanotechnology is relatively new, nanoscale structures had existed for the entirety of life on Earth itself.

Nanoscience is a young field of research that examines materials at extremely small scales and the unique characteristics they exhibit. Nanoscience has the ability to reshape the around us. It might result in discoveries like manufacturing and healthcare. Because nanoscience crosses several disciplines, researchers in physics, chemistry, biology, computer science, medicine, material science, and engineering are researching and applying it to get a deeper understanding of the world around us. Conversely though, nanotechnology, additionally sometimes called molecular manufacturing, is the design, synthesis, and use of systems, tools, and structures at the nanoscale.

Among the most interesting aspects of living in the nanoworld is that, everything behaves in a new way when you approach ultra-small. Especially, the qualities, both chemical and physical alter. On breaking down a bulk material into a nanosized particle, we can alter a lot of its characteristics like the fundamental properties such as color, strength, hardness, crack resistance, melting temperature, and electrical conductivity. It is quite exciting when you take into account that neither the material’s chemical makeup nor its crystal structure are being altered.

The chemical and physical properties alter because we are opening up and exposing more of the surface area of the substance.

A nanoparticle or ultrafine particle is a particle of matter 1 to 100 nanometers in diameter. Now nanoparticles have a wide range of applications in life science, biomedical, healthcare and security as well as the energy generation farming, sustainable energy, energy storage infrastructure and building and construction. The ratio of surface area to volume grows considerably as a particle size is reduced to the nanoscale. Properties including electrical conductivity, melting point, magnetic permeability, fluorescence and chemical reactivity vary as particle size is lowered to nanoscale levels. Solubility is an important property of nanomaterials. All materials thar are nanoscale or that include at least one nanoscale structure, either inside or on their surfaces, are considered nanomaterials. They can be classified as biological, organic, or inorganic.

There are a lot of nanostructures in the nature. Nanoparticles are widely spread across the universe and they are known as the fundamental components in the planet formation process. Several structures such as DNA, viruses and bacteria are nanostructures. Inorganic- organic nanocomposite structures have been built by biological systems to enhance mechanical characteristics as well as chemical, magnetic, and optical sensing in living things. Nanostructure found in nature include organic nanostructures like proteins and chitin (insects and crustacean shells), nanocrystals under chameleon’s skin which enable them to change color in response to external stimuli, nanostructures giving butterfly wings that’s iridescence and gecko’s footpads their sticking ability. Sea spray, volcanic ash, smoke, soils, minerals, salt particles and biogenic particles are examples of naturally occurring nanoparticles. Each type of nanomaterial is distinguished by its unique shape and size, including nanoparticles, nanoplates and nanotubes.

Numerous business and technological sectors, including information technology, healthcare, homeland security, energy, food safety, transportation and environmental research are being improved, if not completely revolutionized by nanotechnology. Our society has benefited from decades of investigation and creation in nanotechnology and nanoscience in both expected and unforeseen ways. There are more than eight hundred nanotechnology- enhanced items available on the market.

1.1 SIGNIFICANCE OF NANSCIENCE

Nanotechnology is said to be projected to hold the key to meet the global energy needs with clean solutions, providing abundant clean water globally, improving the health and longevity of human life, maximizing the productivity in agriculture, making dominant information technology available everywhere and also helping the development of space. Nanotechnology not just represent a single product or a group of products but an entire scientific and engineering field. With the enhanced understanding on the connection between the shape, size, and their physiochemical and biological properties, nanomaterials are said to be the futuristic material for diverse technologies. The potential and current areas include manufacturing, biomedicine, transport, environmental management, sensors, information and communication technology, textiles, defense, skin care and cosmetics

1.2 CLASSIFICATION OF NANOMATERIALS

Nanomaterials are the most technologically advanced materials available today. For practical purposes, the characteristics, makeup and grouping of nanomaterials or nanoparticles are crucial. The main classification is based on the number of dimensions which are not confined to nanoscale.

1. Zero Dimensional Nanomaterials

These are the materials that have all their three dimension in the nanoscale range. That is no dimension is no larger than 100nm. The most typical portrayal of zero dimensional nanomaterials are nanoparticles, rings, fullerenes, atomic clusters and quantum dots.

2. One Dimensional Nanomaterials

These are the materials that have one dimension that extends outside the nanoscale range. As a result, they exhibit elongated, needle like structures. Carbon nanotubes are considered to be the most intriguing linear nanostructures ; they can be filled, surface modified, single or multi-walled. Nanotubes, nanorods, nanowires are examples of one dimensional nanomaterials.

3. Two Dimensional Nanomaterials

Two dimensional materials are materials which have not limited to the nanoscale are two of the dimensions. As a result, they exhibit flat plate-like structures . They can exist in single layered or multi-layered form. Some common examples of two dimensional nanomaterials are nanolayers, nanofilms, nano coatings etc.

4. Three Dimensional Nanomaterials

These materials have all their three dimension out of the nanoscale range. They are additionally referred to as the bulk material. They possess the features of nanoscale. Multi-nanolayers are examples of three dimensional nanomaterials.

1.3 PROPERTIES OF NANOMATERIALS

The properties of nanomaterials differ from those of the bulk materials. The characteristics of the material differ at the nanoscale for the following two reasons:

1. Increased surface area to volume ratio
2. Quantum confinement effect

These factors can change the properties such as resistivity, strength and electrical characteristics of the material.

1.**Increased surface area to volume ratio**

- Nanomaterials have a substantially larger surface area in contrast to the same volume of material generated in bulk form. The surface to volume ratio of a sphere increases as its radius decreases.

- ❖ When a particle's surface area grows its size shrinks.
- ❖ Nanoparticles have a greater surface area per volume in contrast to the larger particles.
- ❖ It makes materials more reactive. Because expansion and chemical reactions that catalyze takes place at the surfaces. When compared to a material made of larger particles, a given quantity of nanostructure form will be significantly more reactive.. This has an impact on their strength and electrical characteristics.

2 . **Quantum confinement effect**

- ❖ The changes introduced in the atomic structure because of the impact of nano length scale on the energy band structure is known as quantum confinement effect.
- ❖ When the particle size is not big enough to be equivalent to the electron wavelength, it is seen.
- ❖ It explains electrons regarding electron energy bandgaps, valence and conduction bands, potential wells and energy levels.
- ❖ Additionally, it describes the constriction of space of pairs of holes and electrons, known as excitons, within a material, where the restriction of the electronic wave function to the physical dimensions of particles results in the discretization of electronic energy levels.

The determination of properties of nanomaterials are made by their crystal structure and size. Some of the properties are as follows:

1.3.1 Electronic and optical properties

The optical and electronic properties of nanoparticles are inter-dependent to each other. Electrodes covered with nanoparticles have already demonstrated superiority over conventional electrodes with the same chemical makeup. The changes are caused by the larger surface area and better conduction. Electrical attributes include characteristics such as resistivity and conductivity. A material's bulk conductivity is independent of the dimensions like diameter or area of cross section and twist in the conducting wire etc. However, it transpires that in the instance of carbon nanotubes conductivity changes with change in area of cross section. Also when a shear stress is applied to a nanotube, it's conductivity varies. A multi-wall carbon nanotube's conductivity differs from that of a single nanotube of the same size. Carbon nanotubes can behave as a conductor or a semiconductor.

1.3.2 Properties of Magnetism

Magnetic nanoparticles are influenced by the magnetic field. Nanoparticles having magnetic properties are employed in the delivery of drugs, bioseparation, therapeutic treatment, in-vitro diagnostics and contrast agent for MRI imaging. These nanometer sized particles are superparamagnetic. In the absence of any magnetic field, it is not magnetic to have superparamagnetic nanoparticles. However, they soon become magnetized in the presence of a magnetic field. They abruptly transform into a non-magnetized condition in zero magnetic field. One of the most crucial characteristics of nanoparticles utilized in biomagnetic separation is superparamagnetism.

1.3.3 Mechanical properties.

The mechanical qualities under different external stresses and situations are known as their mechanical properties. Different materials show different mechanical properties. The primary mechanical characteristics are resilience, hardness, elasticity, ductility, fatigue strength, yield strength and rigidity. Nanoparticle's volume, surface, and quantum effects give nanomaterials their amazing qualities. The addition of nanoparticles to a common material results in a modification of the grain structure, which enhances the grain boundary and develops the mechanical properties of the material.

1.3.4 Physical properties

The major physical properties of nanoparticles are: they are highly mobile in the free state, and, their particular surface areas are relatively huge, and they exhibit quantum confinement effects. Shape, size and the morphological sub-structure are another important parameters of nanoparticles. Nanoparticles have different physical properties with different particle size.

1.4 APPLICATIONS OF NANOPARTICLES

Nanoparticles are used in so many areas of applications like transport, manufacturing, biomedicine, environmental management, sensors, information and communication technology, textiles, cosmetics etc.

1.4.1 Food Industry

So many particles are used in food industry. Among them silver is the most common one. Silver is known for its anti-microbial action and it can be easily impregnated invisibly into almost any product to aid in the destruction of bacteria and virus. This facilitates the production, storing, and preservation of food in the industry. Many food supplements are now available that contain nanoparticles as the main ingredient. The nanoparticles which are most commonly used are copper, gold, silver, and calcium.

1.4.2 Cosmetics

The nanoparticles which are known as fullerenes are being used in cosmetics in the form of face creams to avoid unwanted substances like free radicals, which are believed to cause damage to the skin and body. Titanium dioxide nanoparticles are used in sun creams.

1.4.3 Textile

The textile industry uses nanomaterials to enhance its functionality and intelligence. Nanosilver is used in the textile industry due to its anti-microbial action. Clothes can also be coated with nanofilms to make them water, stain and static resistant.

1.4.4 Medicine

In the medicine industry also silver nanoparticles are in as large scales. Nanosilver kills a variety of harmful microbes and is an effective agent against the MRSA superbug and the HIV virus. Nanoparticles could be helpful in providing sterile equipment, bed and wound dressings that reduce the spread of harmful bacteria.

1.4.5 Electrical and Electronic goods

The nanotechnology has come from the natural evolution of microtechnology for the majority of electronic goods. In order to include more components into an electronic chip to make it more powerful, the components are made to be smaller. The electronic goods which were used in the older times in several micrometer range are currently offered in hundred nanometers. Quantum computing makes use of the quantum mechanical effects available at the nanoscale that gives new methods of performing computational operations.

CHAPTER 2

2. SYNTHESIS AND CHARACTERIZATION TECHNIQUES

SYNTHESIS OF NANOPARTICLES

Mainly there are two approaches of synthesis of nanoparticles. They are Top-Down approach and Bottom-Up approach, which are further classified into physical methods as the top-down approach and chemical and green synthesis methods as the bottom-up approaches.

2.1 TOP-DOWN APPROACHES

The top-down approach refers to the production of nanoparticles from bulk materials. The reduction of particle size is done through different techniques such as fragmentation, cutting or engraving, milling, photolithography etc.

2.1.1 MECHANICAL MILLING

It is the low-cost method to produce nanoparticles from bulk materials. It is a very successful approach for manufacturing phase blends and is beneficial for the growth of nanocomposites. Mechanical milling is used to produce water-resistant spray coatings, oxide and carbide-enhanced aluminium alloys, and some other nanocomposite material. For energy storage and conversion ball-milled nanoparticles of carbon is used.

2.1.2 ELECTROSPINNING

Electrospinning is one of the easiest technique in top-down approaches which is employed for the advancement of nanostructured materials, typically polymers. This method of producing fibers draws charged threads of polymer melts or solutions up to fiber sizes of a few hundred nanometers using electric force.

2.1.3 NANOLITHOGRAPHY

It is the study of fabricating nanostructures with a minimum of 1-D in the size range of 1-100 nanometers. Using a multistep method, it is applicable to create finely defined 2-D arrays on substrates with precisely regulated shape, size, and spacing. Metal nanostructures are fabricated using

Electron Beam Lithography. The ability to modify semiconductor chips at the nanoscale and magnify the field in accordance with application requirements is the primary benefit of this approach.

2.2 BOTTOM-UP APPROACHES

It is a technique in nanotechnology used for nanofabrication which uses physical or chemical forces to construct bigger structures out of simple components at the nanoscale. Bottom-Up approach pertains to the building of a structure atom-by-atom, molecule-by-molecule, cluster-by-cluster. This method uses biological or chemical processes to first generate the nanostructured building blocks, which are then assembled into the finished material. It produces nanostructures with improved short- and long -range ordering, fewer flaws and a more uniform chemical composition. The nanoparticles produced by bottom-up approach are in a state closer to a thermodynamic equilibrium.

2.2.1 SOL-GEL SYNTHESIS

It is the most preferred bottom-up approach because of its simplicity and the majority of the nanoparticles can be synthesized by this method. As the name indicates, sol-gel involves two types of materials or components, ’sol’ and ‘gel’. It is a low temperature process. And it has low energy consumption and low energy pollution. A precursory chemical solution is used in a wet chemical process.

2.2.2 CHEMICAL VAPOUR DEPOSITION

Industry uses this approach because of its economical feasibility, ease of processing, capacity to deposit many types of materials and relatively easy instrumentation. It is a hybrid method using chemicals in vapour phase used to obtain coatings of an assortment of inorganic materials. Under certain deposition conditions nanocrystalline films or single crystalline films are possible.

2.2.3 PYROLYSIS

It is the used method in industries for nanoparticle synthesis. It involves burning a precursor with flame. The precursor is injected into the furnace at high pressure through a tiny hole where it burns and can be either liquid or vapor. The combustion or by-products gas is then air classified to recover the nanoparticles. Some of the furnace use laser and plasma instead of flame to produce high temperature for easy evaporation. It is very simple, efficient, cost effective and continuous process with high yield.

2.3 CHARACTERIZATION TECHNIQUES

2.3.1 X-RAY DIFFRACTION

It is method for figuring out a sample's composition and crystalline structure is X-ray diffraction. The atom structure of bigger crystals, such as macromolecules, can be ascertained using this method. It can determine phase purity, composition of the sample, and crystallinity if the crystal is very small. Using this method, x-ray beams are passed through it. Instead of utilizing considerably longer wavelengths, which would remain untouched by the gap between atoms, x-ray beams are used due to their wavelength is the same as the spacing between atoms in the sample. As a result, the diffraction angle will be impacted by the distance between the atoms in the molecule. After passing through the sample, x-rays "bouncing" off the atoms in the structure cause the beam to change direction at an angle theta from its original beam. While some of these diffracted beams cancel each other out, positive interference happens when the beams have the same wavelength. When two whole number integer x-ray beams at the same wavelength combine to form a fresh beam featuring a larger amplitude, this is known as constructive interference. For this particular angle of diffraction, a larger signal corresponds with a larger wave amplitude. It is possible to calculate the difference between the atomic planes utilizing the Bragg's law, $\sin \Theta = n\lambda/2d$, where θ is the diffraction angle, d is the space between planes of atoms, and λ is the wavelength.

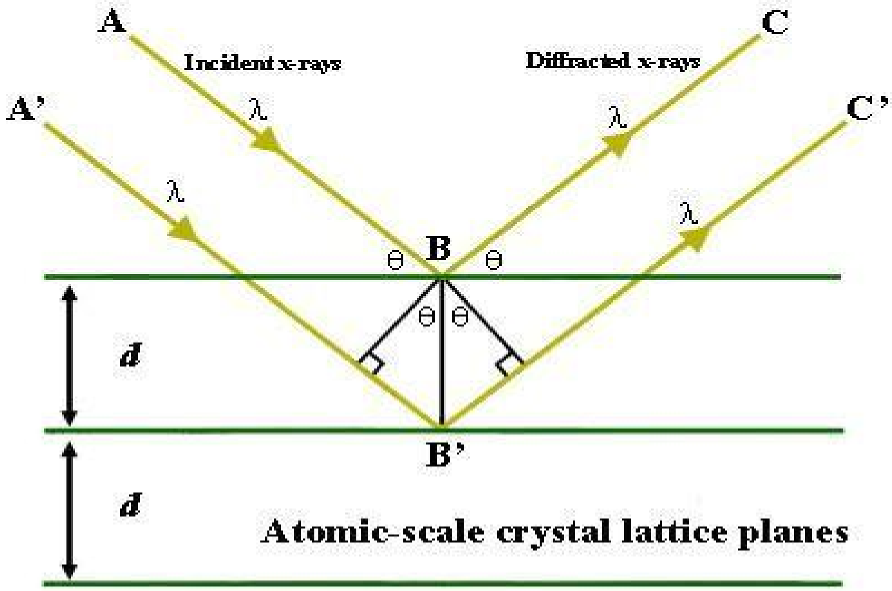

Figure 2.1:- Bragg's Law of reflection. When the distance between pathways ABC and A'B'C' differs by a whole number of wavelengths (λ), the diffracted x-rays show constructive interference.

The Debye Scherrer formula, $\mathbf{D = k\ \lambda/\beta \cos\theta}$, is accustomed to calculate the size of the nanoparticle's crystallite. Where D is the nanoparticle crystallite size, K is the Scherrer constant (0.98), λ is the wavelength(1.54), β indicate the full width at half maximum(FWHM)

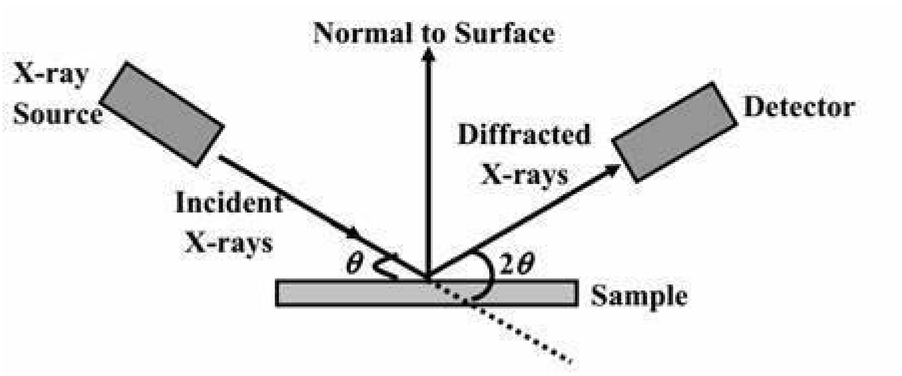

Figure 2.2 :-Schematic representation of working of x-ray diffraction

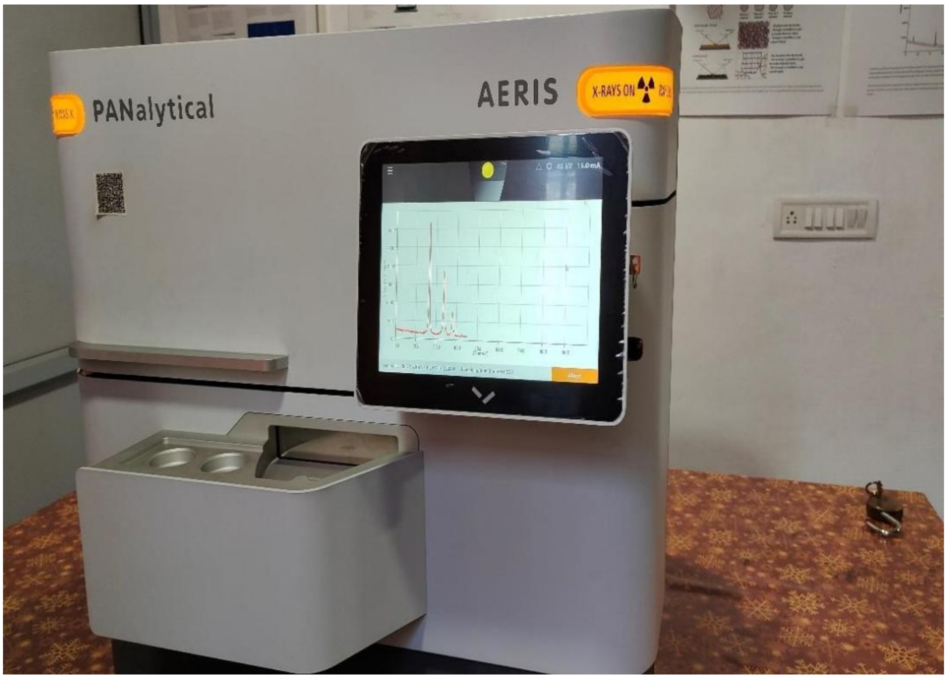

Figure 2.3:- Image of the x-ray diffraction spectrometer in which the characterization was done.

A wavelength- dispersive x-ray spectrometer collects photons that are diffracted by a single crystal in accordance with Bragg's law. It is possible to observe a large portion of the spectrum by adjusting the diffraction crystal and detector in relation to one another.

2.3.2 DIFFUSE REFLECTANCE SPECTROSCOPY

It is a section of absorption spectroscopy. Remission spectroscopy is the another name for diffuse reflectance spectroscopy. Transmission is the movement through a medium, whereas remission is the reverse scattering or the light reflection from a substance. Remission involves both diffusely back scattered and specular light. Reflectance spectroscopy which is closely related to uv-visible spectroscopy, uses visible light to excite valence electrons to empty orbitals. This kind of absorption spectroscopy measures the light that the sample reflects rather than the beam that is transmitted through the sample. Information about the sample's possible electrical or vibrational structure is located in the ensuring spectrum. It is a simple method that uses a light source to illuminate the area, and then a detector gathers the scattered light. Dispersive gratings of the apparatus allow for the simultaneous detection of many wavelengths. One typical method is to employ Kubelka-Munk theory comprehend the scattering and absorption characteristics of the sample under investigation.

The Kubelka- Munk equation is as follows;

$$\mathbf{K / S = (1\text{-}R)^2 /2R = F(R)}$$

Where K = Absorption coefficient

S = Scattering coefficient

F(R) = Remission fuction

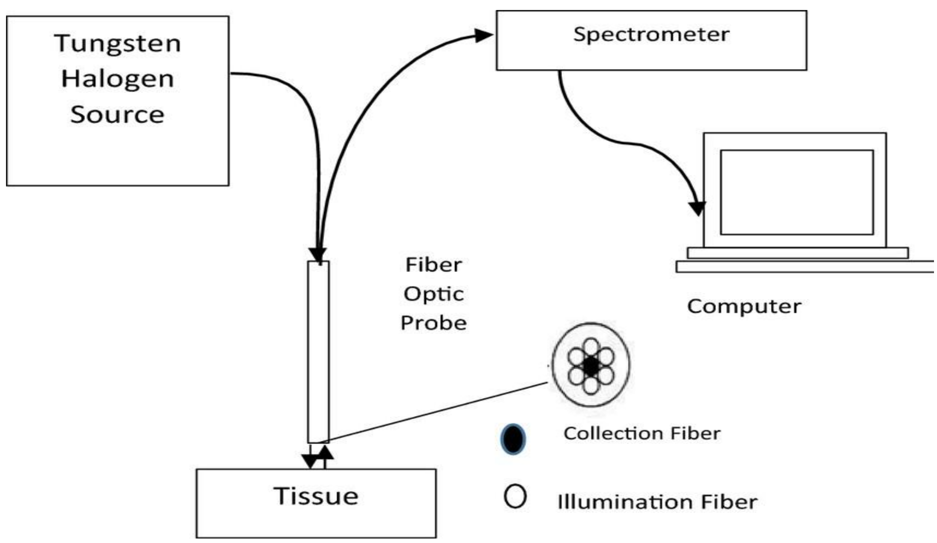

Figure 2.4:- The diffuse reflectance spectroscopy schematic diagram

2.3.2 PHOTOLUMINESCENCE

The release of light from any type of material following photon absorption is known as photoluminescence, i.e. electromagnetic radiation. It is a form of luminescence (light emission)and is initiated by photoexcitation, i.e. photons that raise the energy level of the electrons in an atom. Different relaxation mechanisms that result in the reradiation of other photons usually happen after excitation. The durations of absorption and emission can differ, ranging from milliseconds for phosphorescence processes in molecular systems to femtoseconds for emission involving free carrier plasma in inorganic semiconductors. In certain cases, the delay of emission can even extend to minute or hours. One extremely sensitive method for examining the electronic states in the semiconductor bandgap is photoluminescence spectroscopy. It entails optically stimulating electrons in the semiconductor's valence band to move into the conduction band. It uses photons of a higher energy than the band gap energy. This results in the creation of electron -hole pairs. After sometimes electrons and holes recombine, thereby releasing energy as a kind of phonons or photons.

This technique involves irradiating the sample with a particular light wavelength ,and the intensity of the luminescence emission is recorded as a function of wavelength. The sample's light emission is captured through lenses, dispersed by another monochromator, and detected by a photodetector. The spectrum is obtained between the intensity of emitted PL light and the wavelength of emitted light.

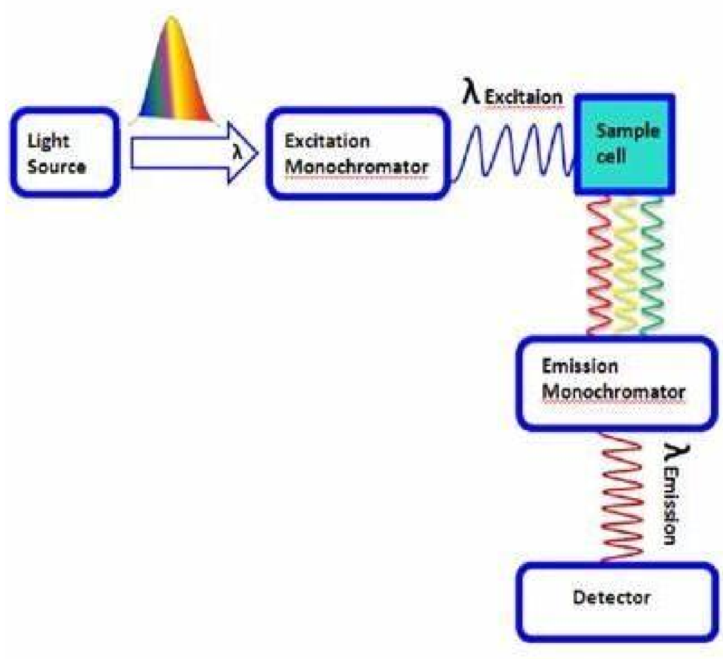

Figure 2.5:- Schematic representation of PL Spectroscopy

2.3.3 EDAX

EDAX stands for Energy Dispersive X-ray Analysis. It is a technique used in analytical chemistry and material science to determine the composition of elements of a sample. It works by bombarding the sample with x rays, which then cause the sample to emit characteristic x rays. Through analysis, we are able to determine and measure the components that are present in the sample. It is commonly used in fields like metallurgy, geology, and forensic science for material characterization and identification.

Figure 2.6:- Image of an EDAX machine

2.3.4 SCANNING ELECTRON MICOROSCOPY

It is a variety of electron microscope which is employed for scanning the surfaces of micro-organisms and uses an electron beam moving at low energy to focus and scan specimens. It was developed to overcome the inefficiency of light microscopes. They have very short wavelengths in comparison to the light microscope which enables better resolution power.

This method allows for the determination of the size, shape and structure of particles using minute samples. It is commonly used to determine the morphology of the prepared sample on the nanometer to atomic scale.

In SEM, a fine beam of electrons pass through the sample, and the electrons interact with the sample then produce a variety of signals which can be detected and displayed on the screen of a cathode ray tube.

The scanning electron microscope works on the principle of applying kinetic energy to make signals on the interaction of the electrons. These electrons are secondary electrons, back scattered electrons etc. These are used to produce an image. Secondary electrons are responsible for identifying the sample’s morphology and topography, whereas backscattered electrons are employed to determine the contrast in the elemental composition of the specimen.

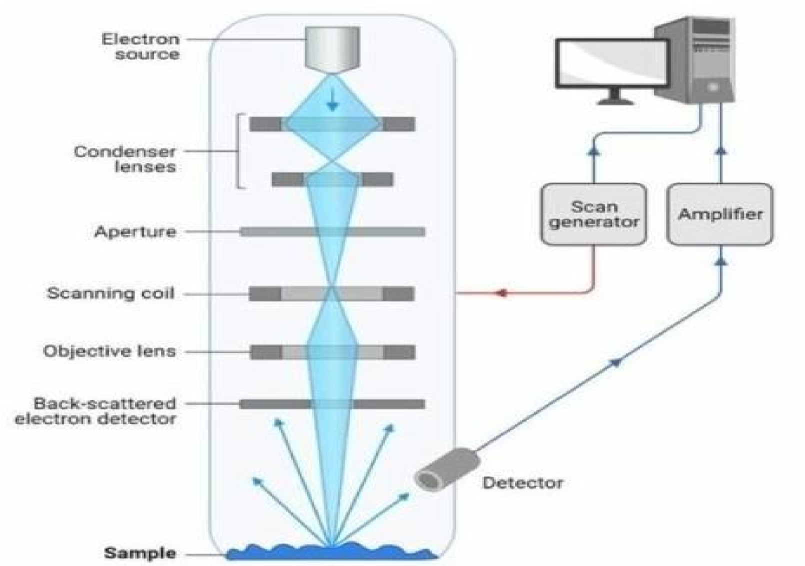

Figure 2.7:- Schematic representation of SEM

The primary parts of the scanning electron microscope are as follows;

- Electron source :- This is the device that generates electrons at a voltage between 1 and 40kV while subjected to thermal heat. The electrons condense into a beam that is utilized for analysis and image creation.

- Lenses :- The electron beams from the source passes through the column and is focused into a narrow beam by means of multiple condenser lenses.
- Detector :- It consists of many detectors that can distinguish between diffracted backscattered electrons, back scattered electrons, and secondary electrons.
- Scanning coil :- The purpose of the scanning coil is to deflect the beam across the specimen surface. The density of the specimen and the voltage speed have a major impact on how well the detectors work.
- The vacuum system.
- Power supply.
- The data output device or display device.

CHAPTER 3

3. INTRODUCTION TO ALUMINIUM OXIDE NANOPARTICLES

3.1 ALUMINIUM OXIDE

Al_2O_3 or aluminium oxide, is a chemical compound made up of aluminium and oxygen. In addition to its usual name, alumina, it can also be known as aloxite, alundum or aloxide. Alpha – aluminium oxide is a naturally occurring mineral that takes the form of corundum, a crystalline polymorphism from which beautiful gemstones like sapphire and ruby are formed.

From a structural perspective, aluminium oxide nanoparticles are a type of porous nanomaterials that are part of the metal oxide nanomaterial family. One aluminium atom is surrounded by six oxygen atoms in this corundum like structure.

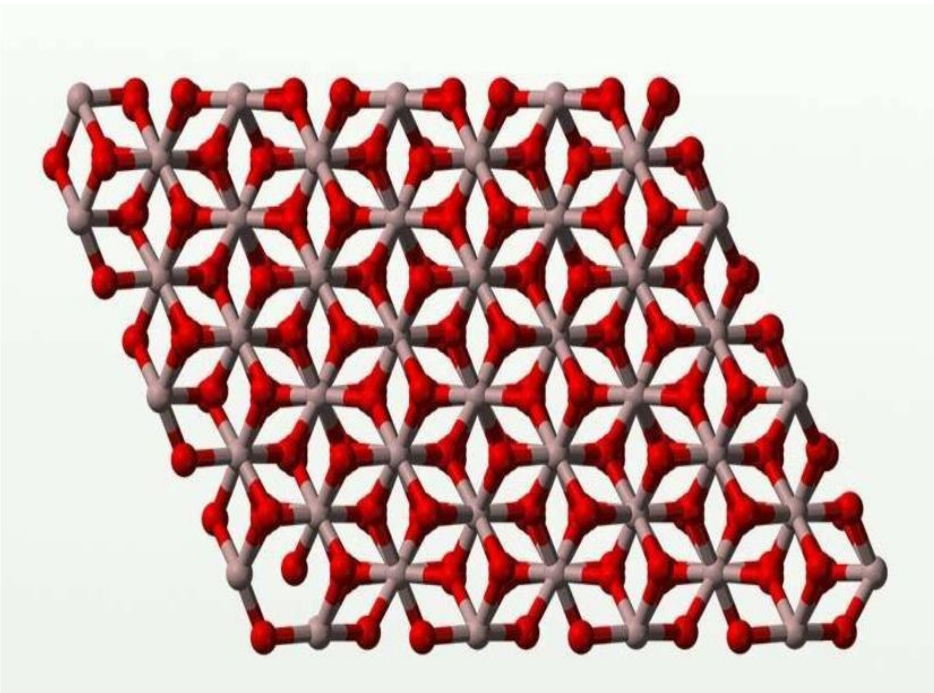

Figure 3.1:- Structure of aluminium oxide

Numerous crystalline phases are known to exist for it, such as the cubic γ and η phases, the monoclinic θ phase, the orthorhombic k phase, the hexagonal χ phase, the monoclinic phase and the δ phase which can be either orthorhombic or tetragonal. But the most thermodynamically stable form is the alpha phase which is hexagonal at elevated temperatures. Each has unique crystal properties and crystal structure. All phases return to the alpha phase at elevated temperatures.

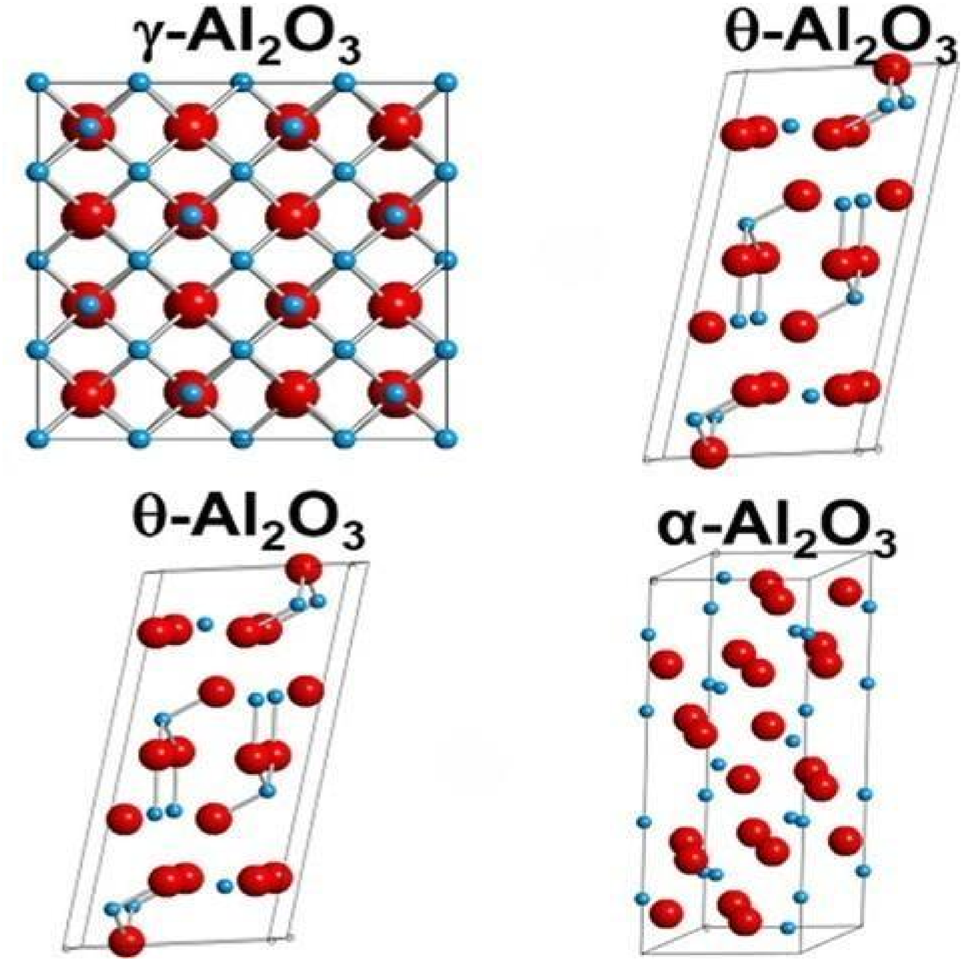

Figure 3.2:- different phase structutres of Al_2O_3

Aluminium oxide nanoparticles are present as a white powder in the shape of spheres. They possess a number of production techniques that enable them them for excellent characteristics that are excessively beneficial and serve as a key to bring forth all the excellent applications that this product offers.

Figure 3.3 :- Image of aluminium oxide nanopowder

3.2 PROPERTIES OF ALUMINIUM OXIDE

- As an insulator of electricity.
- Its heat conductivity is relatively high.
- It cannot dissolve in water.
- Because of its hardness, corundum, also known as alpha aluminium oxide is suited for use like an abrasive
- It is partially soluble in mineral acids and strong alkalis.

3.3 APPLICATIONS OF Al_2O_3

In material science, also refer to it as alpha alumina, and is widely used in ceramic communities and mining. Aluminium oxides are primarily used in ceramics, refrigerators, refinishing and abrasive applications. It is employed in numerous different contexts in which advantages such as its tenderness, electrical resistance and temperature resistance takes place.

3.3.1 GLASS

Al_2O_3 is a component in so many glass compositions. The widely used kind of glass, which frequently has an alumina content of 5% to 10%, is aluminosilicate glass.

3.3.2 GAS PURIFICATION

A common method for extracting water from gas is to employ aluminium oxide.

3.3.3 CATALYSIS

Numerous valuable industrial processes are catalyzed by aluminium oxide. In large scale application such as Claus method for turning refinery waste from hydrogen sulfide into elemental sulfur, Al_2O_3 is used. Moreover, it is employed to dehydrate alcohols to alkenes.

3.3.4 FILLERS

Because it is white and chemically inert, Al_2O_3 is a popular filler for plastics. It is also frequently found in makeup products including blush, lipstick, nail paint and sunscreen.

3.3.5 ABRASION

Al2O3 is also employed for its strength and hardness. Corundum, which is the naturally occurring form of Al_2O_3 is just below diamond in the hardness scale. It is a common abrasive and a less priced alternative to industrial diamond. Aluminium oxide crystals are used in many types of sandpapers. Toothpaste and cutting tools are also made with it.

3.3.6 PAINT

In the automotive and cosmetic sectors, paint is utilized with aluminium oxide flakes to create reflective ornamental effects.

3.3.7 BIOMEDICAL APPLICATIONS

It serves as an example of bioinert ceramics. Applications for alumina ceramics in medicine, owing to its exceptional biocompatibility, wear resistance and high strength, are employed to create artificial joints and bones. It is also employed in the production of joint replacements, dental implants as well as additional medical equipment.

3.4 ALUMINIUM OXIDE NANOPARTICLE SYNTHESIS METHOD

3.4.1 CHEMICAL PRECIPITATION METHOD

Among different strategies in the advancement of nanoparticles, chemical precipitation serves as one of the promising methods to produce the nano catalysts, because it permits the metal ions to precipitate completely. Additionally, this technique is employed to make nanoparticles with a larger surface area. Precipitation method is a commonly used technique for synthesizing nanoparticles through wet chemical synthesis. This method involves the mixing of greater than two precursor solutions that contains the ions necessary for nanoparticle formation. It is possible to precipitate nanoparticles from a solution by adjusting various parameters, including temperature, PH, and reaction duration. A variety of nanoparticles with various sizes, shapes and composition can be created using this method because it is versatile one. Also, it requires careful control of reaction conditions to achieve desired properties and to minimize unwanted byproducts. When the nanoparticles are produced, they are often separated from the solution through processes such as centrifugation or filtration. Following this procedure the nanoparticles could go through additional processes like annealing, drying, or washing in order to enhance their qualities and get rid of any remaining chemicals or contaminants.

Due to its relative simplicity and cost effectiveness, chemical precipitation is employed extensively. And it is also scalable process. It can create nanoparticles of different materials such as metals, metal oxides, and metal sulfides. However, achieving precise control over morphology and nanoparticle size can be challenging. It's important to pay close attention to the choice of precursor chemicals and reaction conditions to remove unwanted byproducts or phase transformations.

After the synthesis, the nanomaterials are typically characterized to evaluate their size, shape, crystallinity, surface chemistry, and magnetic or optical properties. Techniques such as XRD, UV-Visible spectroscopy, SEM, Photoluminescence spectroscopy, EDAX etc. are employed in characterization. By careful control, chemical precipitation method offers a versatile and cost-effective approach for synthesizing nanoparticles with tailored characteristics for a variety of uses involving biomedical imaging, sensing, and drug delivery. Here, the precursors used are Aluminium sulphate and Sodium hydroxide. Mixing these two compounds produces Aluminum oxide. The reaction equation is as follows,

$$\mathbf{Al_2(SO_4) + 6\ NaOH\ \text{- - - - >}\ 2\ Al\ (OH)_3 + 3\ Na_2SO_4}$$

$$\mathbf{Al\ (OH)_3\ \text{- - - - - >}\ Al_2O_3 + H_2O}$$

3.5 PREPARATION OF ALUMINIUM OXIDE NANOPARTICLES AND IRON DOPED ALUMINIUM OXIDE NANOPARTICLES.

Aluminium Oxide nanoparticles and Iron doped Aluminium Oxide nanoparticles were created using Aluminium Sulphate, Sodium Hydroxide, and Iron Chloride using chemical precipitation method. Chemical precipitation method is the widely used technique for synthesizing nanoparticles.

3.5.1 PREPARATION OF ALUMINIUM OXIDE

0.5 molar (31.5 gm) Aluminium Sulphate is dissolved in hundred milliliters of distilled water and stirred thoroughly using a magnetic stirrer until it dissolves. Then slowly added 2 molar (8 gm) of Sodium Hydroxide pellets into the solution and again stirred well until it dissolves. After stirring for a 15 – 20 minutes a white precipitate is formed. The precipitate is filtered using a filter paper and washed with distilled water and acetone, and again filtered it. Then the filtered sample was placed in a preheated hot air oven at 90^0 for 24 hours. After that it was taken outside of the oven and cooled in the air. Then the sample was crushed to make it a fine powder using a clean mortar and pestle. And then it was placed in the muffle furnace for annealing at 800^0 for overnight.

3.5.2 PREPARATION OF IRON DOPED ALUMINIUM OXIDE NANOPARTICLES

Iron doped Aluminium Oxide nano powder was prepared using the same methods. To the mixture of Aluminium Sulphate and Sodium Chloride solution 0.08 gm of Iron Chloride is added and stirred well until it dissolves. It gives a brownish white precipitate. After filtration and washing with water and acetone alternatively, the sample was dried in the hot air oven at 90^0 for 24 hours. Later it was taken out and cooled. Then it was crushed into a fine powder using mortar and pestle. Then it was placed in the muffle furnace for annealing at 800^0 for 24 hours.

The samples that were synthesized, were characterized using Xray Diffraction, UV- Visible Absorption Spectroscopy, EDAX, Photoluminescence Spectroscopy, Scanning Electron Microscopy etc. to analyze their structural and optical properties.

CHAPTER 4

4.RESULTS AND DISCUSSIONS

The chemical precipitation technique was employed to produce Aluminium Oxide and Iron doped Aluminium Oxide nanoparticles. The synthesized sample was then subjected to characterization techniques.

4.1 X – RAY DIFFRACTION

X-ray diffraction provides the information about the crystal structure. It helps in determining the crystallite size, phase composition and lattice parameters. The XRD patterns of the pure and the doped samples are shown the figure. Average crystallite size (D) of the nanoparticle is calculated using the Debye Scherrer formula for all the prepared samples by taking the 2θ value that corresponds to the peak having the maximum intensity.

The pure and doped samples showed the XRD pattern peaks at specific values such as 25.56^0, 43.34^0, 52.56^0, 57.47^0, 66.47^0 and 25.52^0, 43.29^0, 57.42^0, 59.42^0, 66.42^0 respectively corresponding to the planes of (110), (210), (220), (321), and (310) match with the JCPDS file data of Aluminium Oxide. The observed broadening of the peaks is ascribed to the nanoparticle’s tiny size. This broadening effect allows for the estimation of the average crystallite size using the Scherrer formula.

From the peak values, it can be verified the existence of Aluminium Oxide nanoparticles with trigonal structure. The peaks and intensities matched with the standard JCPDS file number 00 101 0951. The typical average size of the pure Aluminium Oxide sample using the Debye Scherrer formula was discovered to be 11.36 nm, while the Iron doped Aluminium Oxide nanoparticles size was revealed itself to be 12.51 nm. This XRD analysis validates the creation of Aluminium Oxide and Iron doped Aluminium Oxide nanoparticles with the desired crystal structure and composition.

The lattice parameter was found using the relation:-

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$$

where h,k,l --> Miller Indices
a --> Lattice Parameter
d --> Interplanar Distance

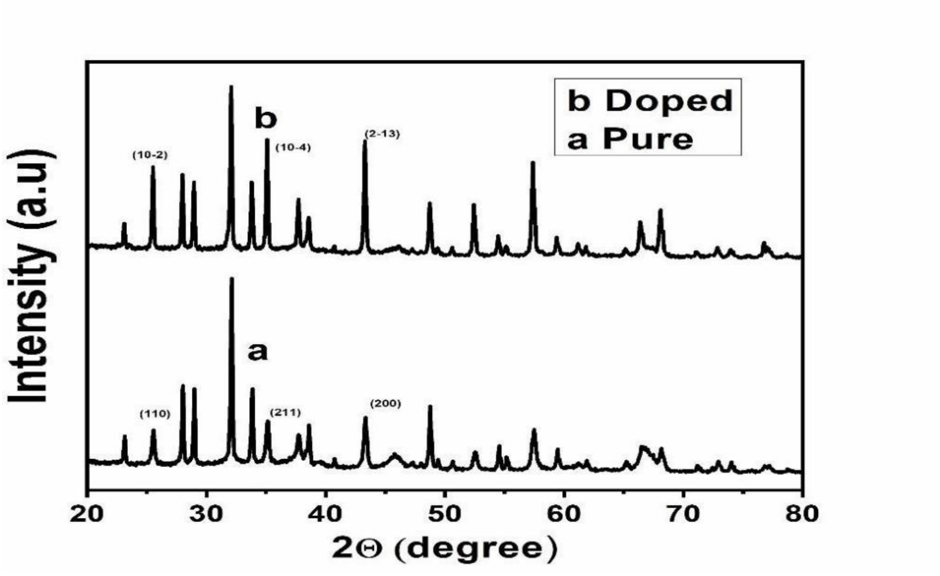

Figure 4.1:- XRD patterns of the pure and doped samples

4.1.1 WH PLOT

From the WH (Williamson-Hall) plot, the mean values of the crystallite size and strain of the pure and doped samples are calculated. 2sinθ and βcosθ values are plotted on x and y axis respectively. It gives a straight line graph which is further linearly fitted providing the crystallite size from the Y- intercept and the strain from the slope of the line.

Williamson-Hall equation is given by,

$$\beta\cos\theta = 0.9/D + 2\xi\sin\theta$$

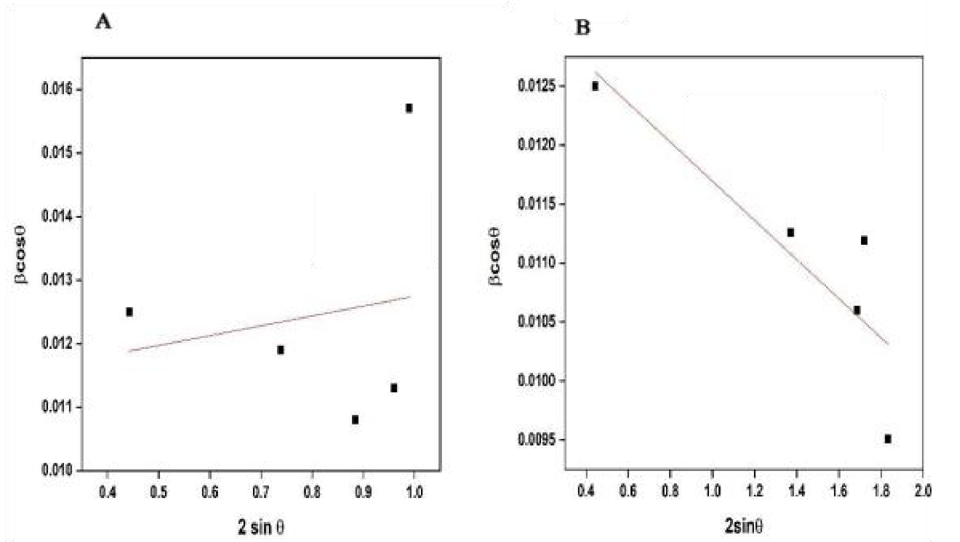

Figure 4.2 :- WH plot A (Al_2O_3) ,B (Al_2O_3Fe)

The pure sample gives a positive slope while the Fe doped sample gives a negative slope due to the compression of the nanoparticle.

The observations regarding the XRD and WH plot are given in the table below:

<u>Structural parameters for Al_2O_3 and Al_2O_3Fe</u>

Sample Name	Average grain size D		Lattice Parameter a	strain
	From XRD	From WH plot		
Pure Aluminium Oxide	11.36	12.37	a = 5.1300	0.00155
Iron doped Aluminium Oxide	12.51	10.38	a = 4.7657	-0.00166

Table 4.1 Structural parameters of the sample

4.2 SCANNING ELECTRON MICROSCOPY(SEM)

The structure and shape of the prepared samples were studied using SEM. The figures below show the morphology and structure of Pure Aluminium Oxide nanoparticles.

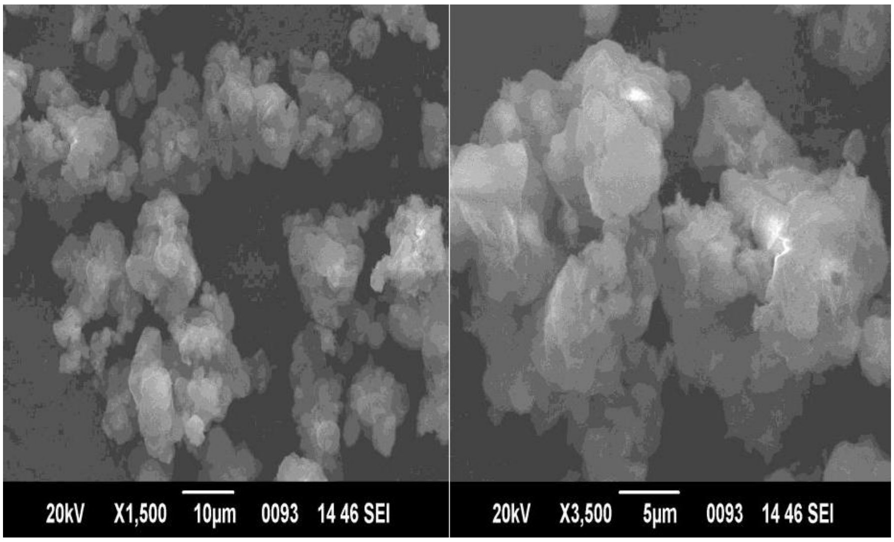

Figure 4.3:- SEM images of pure aluminium oxide sample

In this SEM image individual nanoparticles or small clusters can be observed, displaying well defined sizes and shapes. The lattice fringes are visible indicating the particle's crystalline structure. The SEM image showed that aluminium oxide nanoparticles are almost spherical in shape, irregular and also showed agglomeration of disc shaped nanoparticles. It is typical for Al_2O_3 nanoparticles, because of their elevated surface energy, which causes them to stick together.

4.3 EDAX ANALYSIS

The chemical composition and stoichiometry of the Al_2O_3 sample was determined and confirmed by the EDAX analysis and shown in the figure below. The ratio 2:3 is satisfied for the Aluminium Oxide compound having 60.19% Oxygen and 21.12% Aluminium in the sample nanopowder.

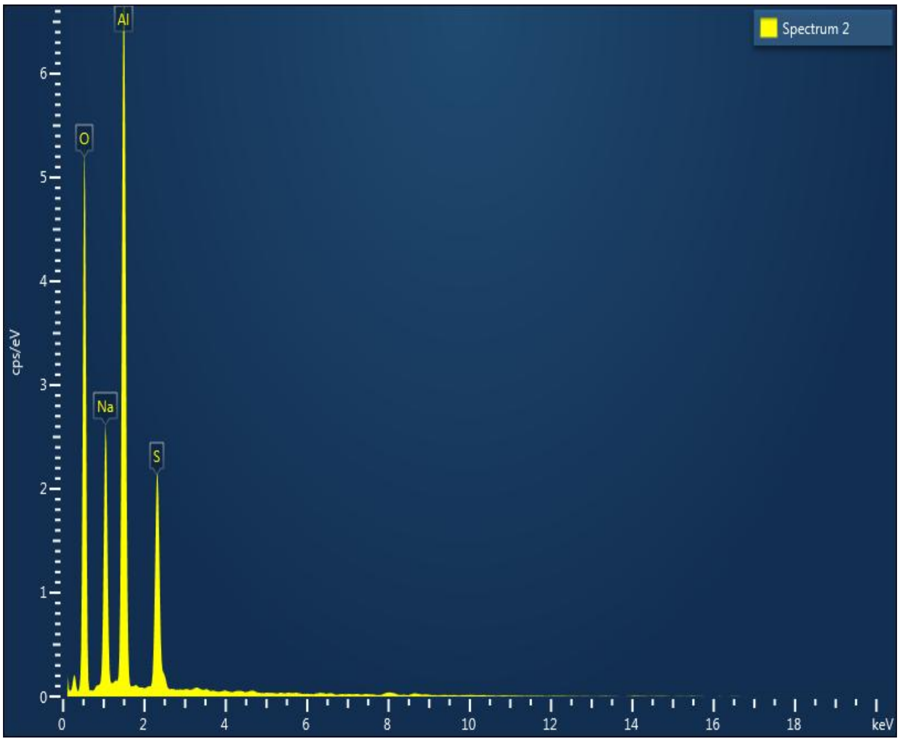

Figure 4.4:- Graph containing the composition of elements of Al_2O_3

4.4 PHOTOLUMINESCENCE ANALYSIS

Figure represents the photoluminescence spectra of Aluminium Oxide and Iron doped Aluminium Oxide nanoparticles at the excitation wavelength of 300 nm. The PL emission spectrum of both the samples shows peaks at 335nm and 385nm. It is fascinating to point out that the first band is sharp and the latter one is broad. The first peak is ascribed due to the defects related to oxygen vacancies and aluminium interstitials. These defects produce localized energy states within the band gap, which can involve in radiative recombination resulting in photoluminescence. The second band must be due to the non-stoichiometry created by the oxygen deficiency in the system. And these bands also arise from the energy transition taking place within the material.

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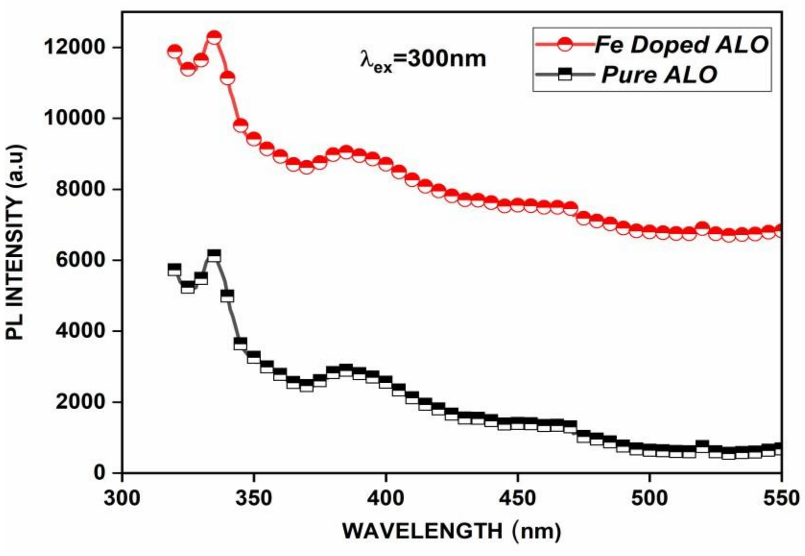

Figure 4.5:- PL spectrum of pure and doped sample

4.5 DIFFUSE REFLECTANCE SPECTROSCOPY

The figure shows the reflectance spectrum of pure and iron doped Al_2O_3 samples. The pure sample shows a 90% reflectance while the doped sample material shows a 50% reflectance. Using the Kubelka-Munk relation the absorption coefficient is found out.

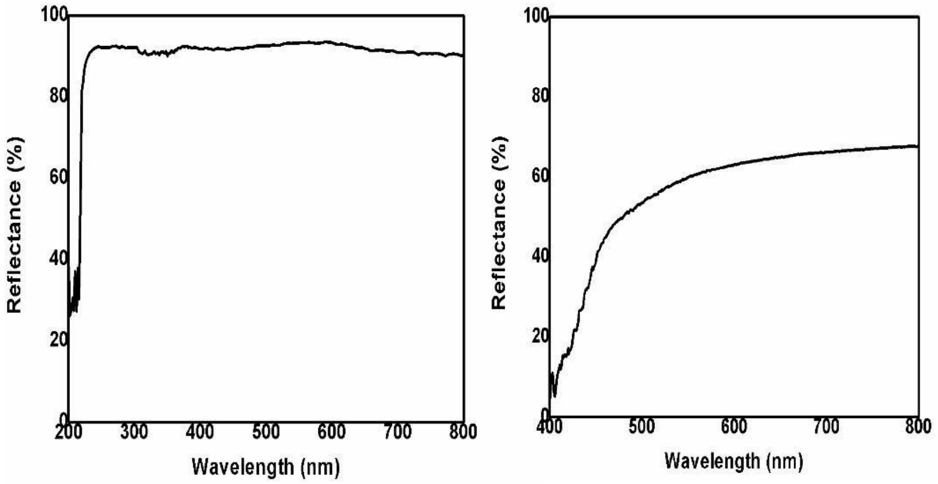

Figure 4.6:- Reflectance spectrum of pure and iron doped Al_2O_3 respectively.

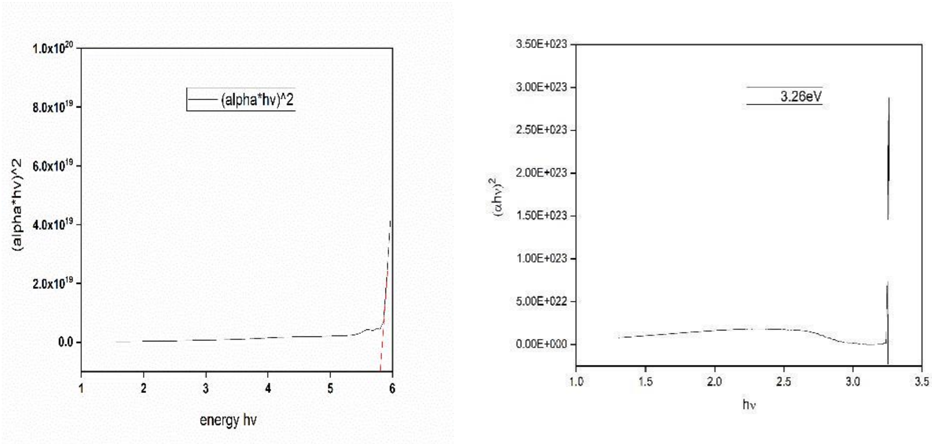

Figure 4.7:- Tauc plot diagram of the pure and doped Al_2O_3 sample

From the Tauc plot diagram, it is discovered that the band gap energy of the pure Al_2O_3 sample is 5.8eV. And the it is also found that the bandgap energy is decreased. The energy bandgap of the iron doped sample is discovered to be 3.26eV.

4.6 CONCLUSION

The Aluminium Oxide nano powderand Iron doped Aluminium Oxide nanopowder was prepared successfully by the chemical precipitation method. The same procedures were used to prepare both samples.

- The structural analysis of the samples was done using X-ray Diffraction technique. It was observed that both the samples have trigonal structure. The average crystallite sizes determined from the XRD observations are observed to be 11.3 and 12.5 for the pure and doped samples respectively. The lattice parameter was also determined from the XRD studies. It is discovered that a = $5.1300A^0$ for pure sample and a = $4.7657A^0$ for the doped sample.
- The morphological studies of the sample was carried out by SEM analysis. The images show highly agglomerated structures of aluminium oxide nanoparticles. It is mostly seen in circular shapes. The composition of elements of the synthesized Al_2O_3 nanoparticles is further confirmed by EDAX analysis for the

presence of Al/O. From the figure Al_2O_3 nanoparticles, Al contains 21.12 at% and O contains 60.19 at% respectively.

- The photoluminescence spectroscopy give the emission spectrum of the sample material. There are two peaks found at 335 and 385 nm respectively. These peaks were the resultant of the energy transition within the material.
- The diffuse reflectance studies provided the energy bandgap of the pure and doped sample materials. The pure sample showed a reflectance of 90% while the doped sample showed a reflectance of 50%. From the graph plotted using Tauc relation, it was found that the energy bandgap for the pure aluminium oxide sample is 5.8eV whereas the band gap energy decreased to 3.26ev due to the dopant effect.

4.8 FUTURE SCOPE OF THE PROJECT

The study of Fe doping on corundum nanoparticles synthesized by the precipitation method has several promising future scopes and potential applications.

- Magnetic properties :- These nanoparticles could exhibit unique magnetic properties, making them useful in data storage and magnetic sensors.
- Catalytic properties :- iron doping might enhance the catalytic properties of corundum nanoparticles making them suitable for applications such as environmental remediation or chemical synthesis.
- Optoelectronics :- The optical properties of Corundum can be modified by Fe doping, which may lead to applications in devices like LED's, lasers and photodetectors.
- Semiconductors :- Fe doped Corundum might show promising electronic properties that could be utilized in semiconductor devices.
- Biomedical Applications (Drug delivery) :- Fe doped nanoparticles could be explored for targeted drug delivery due to their magnetic properties, allowing for controlled drug release using external magnetic fields.
- Imaging :- These nanoparticles can be used as contrast agents in magnetic resonance imaging(MRI) due to their magnetic properties.

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