COLLEGE OF BASIC SCIENCE AND HUMANITIES,OUAT BHUBANESWAR

CERTIFICATE-I

Dr. (Mrs.) Jyoshnarani Mohapatra Date-7th June 2019

This is to certify that the thesis entitled "**SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE OF ZINC FERRITE**" submitted by **Abhipsa Acharya, bearing roll no- 14PHY/17**, for the degree of Masters of science in the subject of physics of College of basic science and humanities, Orissa University of Agriculture and Technology, Bhubaneswar is the result of bonafield research work done under my supervisor. This thesis conforms to standard envisaged by the regulation of the university in my judgment. The work is an original peace of research undertaken by the candidate and the work has not been submitted earlier for any other Degree/Diploma. The thesis presented is adequate and merits consideration for the award of the degree for which it is submitted.

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BHUBANESWAR

DATE-7th June 2019

CERTIFICATE-II

This is to certify that the thesis entitled “**SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE OF ZINC FERRITE**” submitted by **Abhipsa Acharya**,bearing roll no-**14PHY/17** to the College Of Basic Science And Humanities,OUAT,Bhubaneswar in partial fulfillment of the requirement for the degree of Masters of Science in the subject of Physics, has been approved by the Students’ Advisory Committee and the External Examiner.

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This is to certify that the thesis entitled "**SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE OF ZINC FERRITE**" prepared by **Abhipsa Acharya** ,bearing roll no-14PHY/17 under my supervision. This piece of research work is genuine and original. The area of work according to registration is in the field Physics.

(Jyoshnarani Mohapatra)

MAJOR ADVISORY

DECLARATION

I hereby declare that the major thesis entitled “**SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE OF ZINC FERRITE** “ submitted to department of Physics, CBSH, OUAT, Bhubaneswar for the partial fulfilment of the requirement for the degree of Master Science(M.Sc) is an authentic record of the work carried out by me under the guidance of **Dr. Jyoshnarani Mohapatra** Asst. Prof. in Physics, College of Basic Science and Humanities, OUAT, Bhubaneswar, Odisha and that result or any part of the result have not be submitted anywhere for any other degree or diploma or any other qualification.

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ABHIPSA ACHARYA

ABSTRACT

Ferrite nanoparticles have engaged considerable attention in the recent times owing to their incomparable biological applications and also viability in the scientific and technological areas of research. Nanosized spinel ferrites are the most rivet class of materials, that have significantly modulated the consideration of research humanity due to their exceptional structural, optical and magnetic properties. These properties are catered in ($ZnFe_2O_4$) which make it an appropriate contender in the field of electronics, areas of applied optics and telecommunication. A plausible and economically viable co-precipitation method has been the center of attention in recent years to synthesize these nanoparticles. The synthesized samples are characterized by powder X-ray diffraction which evidenced the prevalence of sharp diffraction peaks, attributed to its significant crystalline nature and crystallite size has been estimated to be 11.04 nm. ($ZnFe_2O_4$) nanoparticles with diameter of ca.10 nm were successfully synthesized under hydrothermal conditions without using any surfactant or structure-directing agents. The structure, composition and morphology of the samples were characterized by means of powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (SEM). Fine particle ($ZnFe_2O_4$) powders have been prepared by the low temperature process without any intermediate phase formation. The precursor was prepared and fired at low temperature to form the desired product. Very pure, fine, monophase ZnFe2O4 powders were obtained by the calcination of the precursor in air to about 450°C for 2 h. The IR and EPR characteristics of the fine powders are presented and discussed in terms of the particle size effect. UV–vis spectral analysis (UV-vis) reveals the optical property.

CONTENTS

CHAPTER-1

1.1 INTRODUCTION-

Over the last three decades nanoparticles have received an increasing amount of research interest. This is due to unique size dependence peoperties of nanoparticles which are often thought as a separate and intermediate state of matter lyinf between individual atoms and bulk material. Nanomaterials having a length scale less than 100nm, have received increasing interest owing not only to their fundamental scientific significance but also to the potential applications that derived from their fascinating electrical ,magnetic,optical and catalytic propertyies. Compared to bulk active electrode materials,the corresponding nanomaterials possesses more excellent electrochemical activity,such as higher capacitors,larger surface areas and lower current densities. There by nanomaterials have wildly potential application in electrochemistry field. Nano-sized materials are new substances quickly developed and generally measured as 1 to 100nm size in 1D. At a nanometer scale,the surface area increases hastily as particle size decreases as a result the electromagnetic,thermal,optical,and mechanical properties of nano materials modify.

Zinc ferrites are a series of synthetic inorganic compounds of zinc and iron (ferrite) with the general formula of $Zn_XFe_{3-X}O_4$. Zinc ferrite compounds can be prepared by aging solutions of $Zn(NO_3)_2$, $Fe(NO_3)_3$, and triethanolamine in the presence and in the absence of hydrazine, or reacting iron oxides and zinc oxide at high temperature. Spinel (Zn, Fe) Fe_2O_4 appears as a tan-colored solid that is insoluble in water, acids, or diluted alkali.Because of their high opacity, zinc ferrites can be used as pigments, especially in applications requiring heat stability. For example, zinc ferrite prepared from yellow iron oxide can be used as a substitute for applications in temperatures above 350 °F (177 °C). When added to high corrosion-resistant coatings, the corrosion protection increases with an increase in the concentration of zinc ferrite.A recent investigation shows that the zinc ferrite, which is paramagnetic in the bulk form, becomes ferrimagnetic in nanocrystalline thin film format. A large room temperature magnetization and narrow ferromagnetic resonance linewidth have been achieved by controlling thin films growth conditions.

In recent years, nanosized materials have been extensively studied by researchers worldwide because of their unique physical properties, such as electrical conductivity,optical bandgap, refractive index and magnetic properties, and superior mechanical properties such as hardness of nanomaterials and chemical properties compared with their counterpart bulk materials (Martin 1994). As the research community is gaining a deeper understanding of these unique behaviours and applications of nanostructured materials, a new field of study known as 'nanotechnology' has emerged (Bhattacharyya et al 2001; Kondic and Diez 2009). Among various nanomaterials, mainly spinel ferrite (MFe_2O_4, M = Ni, Co, Mn, Zn, etc.) nanoparticles have become immensely popular magnetic materials for a wide variety of applications such as electronic ignition systems generators, vending machines, medical implants, wrist watches, inductor core, transformer circuits, magnetic sensors and recording equipment, telecommunications, magnetic fluids, microwave absorbers and other

high-frequency applications (Snelling 1989; Jiles 1991; Willard et al 2004; Mathew and Jiang 2007). A distinct merit of ferrites over other magnetic materials such asiron and metallic alloys is their high electrical resistivity due to which ferrites perform much better at high frequencies. High electrical resistivity prevents induction of eddy currents and the resultant loss of energy. High permeability and temperature stability are other advantages.In addition, ferrites are more economically viable than most f other magnetic materials, and their magnetic and mechanical properties can be 'tailor made' as per the requirement of application.

Zinc ferrite ($ZnFe_2O_4$) is a commercially important material and has been widely used as magnetic materials(Tanaka et al 1998; Sousa et al 2001; Grasset et al 2002;Kundu et al 2003a; Bid and Pradhan 2003; Ehrhardt et al 2003; Deng et al 2005), gas sensor (Niu et al 2004), catalysts (Toledo-Antonio et al 2002), photocatalysts (Qiuet al 2004), absorbent materials (Pineda et al 1997;Kobayashi et al 2002a, b; Tomás-Alonso and Palacios Latasa 2004; Ikenaga et al 2004) and so on.

The metal spinel ferrites belong to the face centered (fcc) close packing structure of AB_2O_4 type in which A occupies tetrahedralsite, B occupies octahedral cationsite and O occupies the oxygen anionsite2 . Among the spinel ferrite compounds Zinc Ferrite ($ZnFe_2O_4$) exhibits superparamagnetic behavior and it has potential application in many fields, such as photocatalysis , magnetic resonance imaging (MRI)$_4$, Li-ion batteries5 and gas sensors. Various synthesis methods are proposed to prepare $ZnFe_2O_4$ nanoparticles such as co-precipitation , combustion , thermal decomposition , solvothermal , hydrothermal , ball milling, and ceramic route techniques. Among the synthesis methods the hydrothermal method has been widely used, because of its simplicity, low cost, nontoxic route and yields crystalline nanomaterials in a short time. In this work superparamagnetic $ZnFe_2O_4$ nanoparticles were synthesized by hydrothermal method using the capping agents Poly Ethylene Glycol (PEG) and Ctyl Trimethylammonium Bromide (CTAB)). The effect of the PEG and CTAB capping agents on the structural, optical, morphological and magnetic properties of the prepared $ZnFe_2O_4$ nanoparticle is presented.

1.2AIM

The aim of this project is to synthesize and characterize nano-zinc ferrite nano-particle.

1.3 JUSTIFICATION OF THE STUDY

With the advancement of science and technology, and the evolution of nanotechnology, researchers in the field of material science called for research into nanomaterial due to the improvement in properties of material shown by nanomaterial to those of larger scale. In this project, Nano-zinc ferrite is being looked into, due to the improvement in the properties shown by it to ordinary zinc ferrite. Also, the heat required for calcination of zinc ferrite, has been found to be much more less when it comes to the calcination of the Nano-Zinc Ferrite.

1.4 SCOPE OF THE STUDY

The scope of this research work is to synthesize a nanomaterial (Zinc Ferrite) via sol-gel synthesis and characterize it for it morphology, fiber size and pore size and band gap.

CHAPTER-2

2. REVIEW OF LITERATURES

Nanoscience and nanotechnology are involved in the manipulation of materials and the creation of structures and systems at the nanometer scale. As a result, nanomaterials have attracted much attention because of their surface effect (large surface-to-volume ratio) and quantum confinement effects (size-dependent properties). These factors affect their physical and chemical properties, which differ from the properties of their molecular and bulk counterparts. Nanoparticles with zero-dimensional nanostructures are generally classified according to their compositions, that is, metal oxides, noble metals, transition metals, magnetic metals, and semiconductor nanomaterials or quantum dots. Like all nanostructures, magnetic metals nanoparticles are dependent on their size and shape. Currently, magnetic oxide nanoparticles are attracting significant interest due to their extensive applications, ranging from fundamental research to industrial use. Spinel nanocrystals are regarded as two of the most important inorganic nanomaterials because of their electronic, optical, electrical, magnetic, and catalytic properties. Spinel nanocrystals are regarded as two of the most important inorganic nanomaterials because of their electronic, optical, electrical, magnetic, and catalytic properties. Spinel has the structure AB_2O_4 in which A and B display tetrahedral and octahedral cation sites, respectively, and O indicates the oxygen anion site. Metal spinel ferrite nanoparticles have the general molecular formula MFe_2O_4 (e.g., M = Ni, Zn, Mn, Co, or Mg), and they have a facecentered-cubic (fcc) close packing structure. Among the spinel ferrites compounds, zinc ferrite, manganese ferrite, and nickel ferrite have been studied extensively due to their different structures composed of inverse, normal, and mixed spinel structures, respectively, and their high electromagnetic performance, excellent chemical stability, mechanical hardness, low coercivity, and moderate saturation magnetization, which make it a good contender for the application as soft magnets and low-loss materials at high frequencies . These properties are dependent on the chemical composition and microstructural characteristics in which the particle size and shape might be controlled in the fabrication processes. In order to achieve materials that have the desired physical and chemical properties, the preparation of spinel ferrites nanocrystals through different routes has become an essential focus of the related research and development activities. Various fabrication methods to prepare spinel ferrites nanocrystals have been reported, for example, sol-gel methods , the ball-milling technique , coprecipitation , polymeric-assisted route , the hydrothermal method , the reverse micelles process , and the microemulsion method . Various precipitation agents have been used to produce specific size and shape spinel ferrites nanocrystals, for example, metal hydroxide in the coprecipitation method, surfactant and ammonia in the reverse micelles process and various microemulsion methods, and organic matrices in the sol-gel method.

Most of these methods have achieved particles of the required sizes and shapes, but they are difficult to employ on a large scale because of their expensive and complicated procedures, high reaction temperatures, long reaction times, toxic reagents and by-products, and their potential harm to the environment. In the present study, spinel ferrites nanocrystals with different structures were prepared from an aqueous solution containing metal nitrates, poly(vinyl pyrrolidone), and deionized water using a low temperature thermal treatment method, followed by grinding and calcination.

2.1 METHOD OF SYNTHESIS

There are different methods of synthesis used in the fields of solid state chemistry, one of the most used is that known as ceramic method. The ceramic method consist of the grinding of the stoichiometric quantities of the corresponding starting compound and subsequent heating by using furnace at relatively high temperature, however, it is not the most efficient method.

2.1.1 Ceramic method

The well-known ceramic method of the mixing and grinding of the starting compounds in stoichiometric quantities, being afterward heated in furnace at a relatively high temperature for relatively long dwelling time. Eventually, the desired material will be obtained, with a smaller or higher grade of impurities. The main disadvantage of this method is the low homogeneity of the obtained product, which demands repeated procedures of intermediate homogenization and thermal treatment at high temperature. Thus the method requires the grinding (intermittently) of the material during the heating treatment in order to minimize the drawback created by the interface resulting of the reaction between the starting reagent (Witze, 2010).

2.1.2 Sol-gel method

The sol-gel method is a wet-chemical process widely used in the field of material science. The starting point is the colloidal solution (sol) that acts as the precursor for an integrated network (gel) of either discrete particles or network polymers. Spinel can be synthesized starting from the oxide or salts of the different metals wanted to be part of the final structure by dissolving them in a solution containing a complexing agent (citric acid) and heating it up to the decomposition of the organic part and therefore to the formation of a fine and intimate distribution of the different metals in the resulting precursor, meaning there is a high contact surface between them allow a more efficient reaction at a relatively high temperature and a prudent dwelling time (Rao and Gopalakrishnan, 1997).

2.1.3Freezing-drying method

The freezing-drying method, also known as lyophilisation, is a process consisting of the freezing of the solution of the starting, under pressure to allow the frozen solvent to sublime directly from the solid phase to the gas phase. In the lab, the process is carried out by placing the solution in decantation funnel and dropping it slowly in a container with liquid nitrogen in order to freeze it in small rounded “grains”. Right after the dropping ends, the freeze ‘grains’ of solution are placed in an Erlenmeyer flask which is immediately connected to a freeze-dryer. Now the freeze-dryer will carry out its function: to provoke the sublimation of the solvent. For that, the frozen solution undergoes an important vacuum created by a pump, allowing the solvent sublimate and the latter frozen once again into a big drum at a low temperature inside the device. After one/two days the dried solution- called now precursor – is disconnected from the freeze-dryer and treated at certain temperature in order to allow the reaction between different reagent which are mixed in extremely fine and close way. This method allows much lower both dwelling times and heating temperatures, at the time that makes easier the way to get pure phase (Ibberson and David, 2002).

2.1.4 Melt method

One method often employed is to melt the reagent together and then later anneal the solidified melt. If volatile reagent are involved these are usually put in an ampoule that is evacuated (the reagent mixture is kept cold- by keeping the bottom of the ampoule in liquid nitrogen) and then sealed. The sealed ampoule is then put in an oven/furnace and given a certain heat treatment (Gedanken, 2004).

2.1.5 Pechini method

Pechini method is widely used method consisting of the mix of a metal nitrate solution of the starting materials with a stoichiometric amount of citric acid. The resulting solution is stirred on a hot plate and the temperature stabilized at about 90^0C, at which point ethylene glycol is added at a mass ratio of 40:60 with respect of citric acid. The temperature is maintained constant up to the resin formation, which polymerizes at about 300^0C. The precursor powder is heated for several hours at various temperatures. The method, as a soft-chemistry one, leads to homogeneous andlow crystalline products at relatively low temperature, but they usually require expensive initial compounds and/or complicated synthesis procedures (Lozano-Gorrin *et al.*, 2007).

Some relatively new methods are worth being mentioned, like the solution combustion method, the sono chemical method, and the microwave assisted synthesis.

Solution combustion method

Combustion synthesis is an effective, low-cost method for production of various useful materials. Today, it has become very approach for preparation of nanomaterial. Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of variety of nano size materials. Depending on the type of the precursors, as well as on conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes. This process not only yields nanosize oxide materials but also allow uniform (homogeneous) doping of trace amounts of rare-earth impurity ions in a single step (Patil *et al.*, 2002).

Microwave assisted method

Microwave heating allows a rapid heating rate, however, the final yield decreases compared with the conventional methods. It leads to the synthesis of materials with consumption of less energy (Gomez-Cuaspud *et al.*, 2010).

Sonochemical method

The sonochemical method is that in which the molecules undergo a chemical reaction due to the application of power ultrasound radiation (2 kHz-10MHz).Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy per molecules (Rodriguez-Calvajal, 1993).

2.2 Structure of Zinc Ferrite

The structure of the spinel oxides AB_2O_4 consists of a close-packed FCC arrangement of oxygen atoms, with two nonequivalent crystallographic sites (A and B) in the structure3 . For $ZnFe_2O_4$, the Zn^{2+} and Fe^{3+} distribution at A and B sites within the structure can be represented by the formula $[Zn_{\delta}Fe_{1-\delta}]$ A$[Zn_{1-\delta}$ $Fe_{1+\delta}]$ B O, where δ is the inversion parameter. Values from $\delta=1$ (normal) to $\delta=0.21$ are reported in the literature, depending on the synthesis method4-6 . For samples with $\delta=1$, antiferromagnetic order of the Fe ions appears below TN = $_{9-11}$ K[4,7,8]. This low ordering temperature compared to other MFe_2O_4 spinels with magnetic M (for which TC ~ 500-800 K_3) is due to the weak J_{B-B} super exchange interactions between Fe sites, in contrast to the J_{A-B} stronger interactions.

Since ferrites behave as low gap semiconductors and as insulators at low temperatures they have been used in a number of technologically important applications. Among these are microwave devices, magneticand magneto-optic recording, and electronic information mass storage.The spinel ferrite has AB_2O_4structure with a cubic close-packed arrangement of oxygen ions, with $A^{2+}$and B^{3+}ions at two different crystallographic sites. These sites haveAO4tetrahedral and BO6octahedral oxygen coordination (Aand B sites, respectively). Accordingly, the resulting local symmetries of both sites are different. In this regard the spinel structure can be defined and described by three parameters: the lattice parameter a, the oxygen positional parameter u, and thecation inversion parameter i. Consequently the ideal chemical formula of spinel takes the form $A^{2+}OB^{3+}{}_2O_3$, where A^{2+}=Mg, Mn, Fe, Co, Ni, Cu, or Zn, and B^{3+}= Al,V,Cr,Mn,Fe,Co, or any closely related structure. When A is a magneticion, the total magnetic moment of the eight blocks that

form the unit cell in $AB_2O_4$is due to uncompensated magnetic moments of the A and/or B magnetic sublattice. According tothe strength of A-A or A-B interaction the materials behaveas either ferromagnetic or antiferromagnetic, respectively. $ZnFe_2O^4$is well known as an antiferromagnetic insulator,with a low ordering temperature of TN= 10.5 K and anenergy gap of about 0.2eV.6It has a complex spin structure,where the spin structure becomes simpler with higher ordering temperatures in samples with inter site cation disorder .Cation disorder for $ZnFe_2O_4$was experimentally observed addition the magnetic moment of Fe in $ZnFe_2O_4$is around 4.2μB(Refs. 9 and 10) and the experimental lattice parameter is about 8.52˚A(Ref.11).Previous studies utilizing the generalized gradient approx-imation (GGA) and the local spin density approximation(LSDA), without Hubbard correlations, indicated that normal $ZnFe_2O_4$ shows metallic behavior either for the ferromagnetic state or for the antiferromagnetic state.6In this work we aim to describe the effect of symmetry on the properties of $ZnFe_2O_4$ spinel ferrite. Calculations are carried out for different allowed symmetries and cation distributions. In addition the deviation of the oxygen positional parameter from the ideal value is calculated. The on-site3d-electron Coulomb interaction for Zn and Fe is also included.

2.3 Structural characterization of zinc ferrites.

Doping ferrite nanocrystals with various metals, such as chromium, copper, manganese, and zinc are usually used to improve some of their electric or magnetic properties . For example, Zn ferrites have applications as soft magnetic materials with high frequency (due to high electrical resistivity and low eddy-current loss .Along that line, (Cu, Zn) ferrites offer a further improvement as softer magnetic materials . In this exhaustive characterization, various techniques are employed such as X-ray diffraction (refined with the Rietveld method with the MAUD software), Field-Emission Scanning Electron Microscope (FE-SEM), Fourier Transform Infra-Red (FTIR) spectroscopy, and UV-Vis spectrometer at room temperature. We thus compare the effect of dopings not only regarding structural and magnetic properties, but also in the sense of optical properties. In addition.

A prime method to characterize the reaction product is X-ray diffraction (XRD), because many solid state reactions will produce polycrystalline powders. Thus, powder diffraction will facilitate the identification of known phase in the mixture. If a pattern is found that is not known in the diffraction data libraries an attempt can be made to index the pattern, i.e. to identify the symmetry and the size of the unit cell. Obviously, if the product is not crystalline enough the characterization is typically much more difficult (Larson, 2000).Once the unit cell of a new phase is known, the next step is to establish the stoichiometry of the phase. This can be done in a number of ways. Sometimes the composition of the original mixture will give a clue, if one finds only one product a single power pattern- or if one was trying to make a new phase of a certain composition by analogy to known material but this is rare. Often considerable effort in refining the synthesis methodology is required to obtain a pure sample of new material. If it is possible to separate the product from the rest of the reaction mixture elemental analysis can be used. Another way involves SEM and the generation of characteristic X-ray in the electron beam.

The easiest way to solve the structure is by using single crystal X-ray diffraction. The latter often require revisiting and refining the preparative procedures and that is linked to the question which phases are stable at what composition and what stoichiometry. In other words what does the phase diagram look like? An important tool in establishing this is thermal analysis techniques like the synchrotron temperature-dependent power diffraction. Increased knowledge of the phase relation often leads to further refinement in synthesis procedures in an iterative way. New phases are thus characterized by their melting point and their stoichiometric compounds. The latter is important for many solid that are non-stoichiometric domains. The cell parameters obtained from XRD are particularly helpful to characterize the homogeneity range of the latter.

In order to analyze the different morphological and surface characteristics of particles in the perovskite, SEM (Scanning Electron Microscopy) can be used (Navrotsky, 1998).

2.4 Application

Spinel ferrites, with common formula of MFe_2O_4 (M: a divalent metal ion), have wide technological applications, e.g., in multilayer chip inductor (MLCI), ferrofluids, high-speed digital tape or recording disks, rod antenna, and humidity sensor . Ferrite nanocrystals are also of interest in various applications, such as inter-body drug delivery , bioseparation, and magnetic refrigeration systems , in particular due to their specific properties, such as superparamagnetism. In addition, among ferrospinels zinc ferrites are used in gas sensing , catalytic application , photocatalyst , and absorbent materials . Because of their high opacity, zinc ferrites can be used as pigments, especially in applications requiring heat stability.

CHAPTER-3

3.0 MATERIALS AND METHOD

All reagents used in this work were of analar grade except stated otherwise, and were used without further purification. All glass wares used in this work were properly washed, rinsed with distilled water and dried in the oven. Electric balance model Kerro BL3002 Electronic compact scale was used for all weighing. Drying oven model number 0607034, Cole medical England was used for drying. Hams constant temperature magnetic Stirrer was used for heating. While the morphology, pore analysis, and fiber analysis were recorded using Phenom proX Scanning Electron Microscope. Titanium tetrachloride used was from Baker analysed reagent, while nitric acid was from Philip harris limited England.

3.1 Preparation

single phase zinc ferrite ($ZnFe_2O_4$.) nanoparticles with a mean crystallite size of 12 nm were successfully prepared just by high energy wet milling of metallic Zn and Fe powders and water as the raw materials, without any subsequent heat treatments. Variation of the magnetization with respect to temperature was studied by Faraday balance. Room temperature M–H curve of the as-milled powder has an s-shape, which shows it has ferrimagnetic order. To investigate the effect of annealing on magnetic properties of the as-milled powder, it was annealed at different temperatures from 150 to 800 °C and characterized by XRD and magnetometry. The results show that cation distribution of the as-milled nanoparticles is different from that of the bulk zinc ferrite (normal spinel) and by annealing it changes drastically, and finally, it changes to that of the bulk one.

3.2 Powder synthesis

The precursor materials used for the synthesis of nano- $ZnFe_2O_4$., were zinc Acetate and Iron Nitrate with PEG in a weight ratio 1 : 1 : 5, respectively, and ground well with a mortar and pestle. The resultant solid was placed in a silica crucible and heated in air. It was observed that initially PEG melted, then frothed and finally ignited to give $ZnFe_2O_4$.as a residue. On cooling to room temperature, no traces of carbon impurities were observed in the final residue of $ZnFe_2O_4$.. As the reaction is fast, i.e. going to completion within 10 min, and ignites auto-catalytically, the exact temperature of the reaction could not be measured. However, using a thermocouple the highest temperature of the reaction was found to be around 500°C. The $ZnFe_2O_4$.was then characterized for its structure (employing XRD), morphology (employing SEM).

3.3 Powder characterization

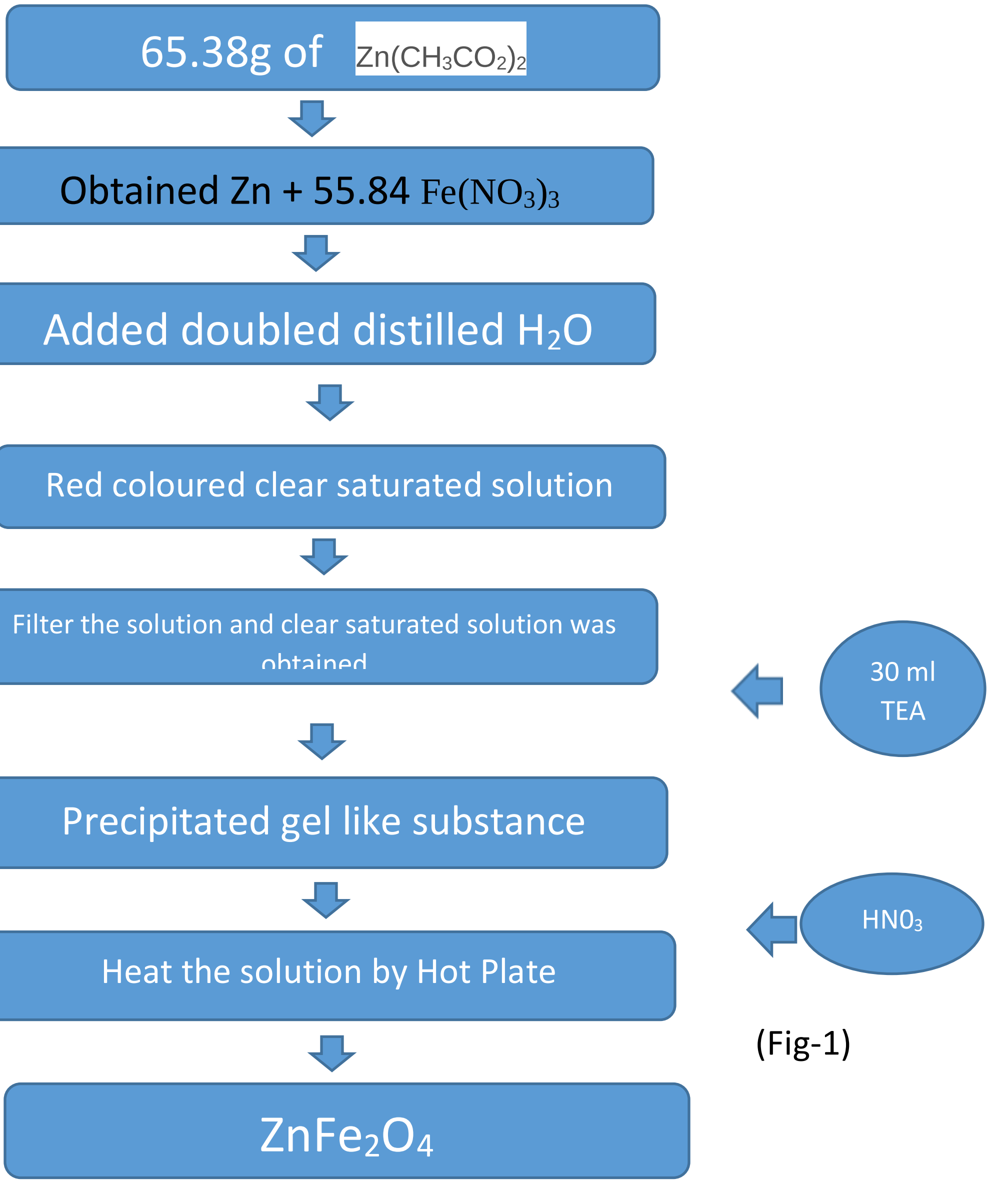
The calcined powder was characterized by different characterization techniques to study the composition, morphology, fiber and pore size. These were investigated by Phenom proX scanning electron microscopy.

CHAPTER-4

4. EXPERIMENT

65.38g of $Zn(CH_3CO_2)_2$ was taken to obtain 2.136g of Zn and 55.84g of $Fe(NO_3)_3$ was added to it. Then double distilled water was added to it and 4 to 5 drops of HNO_3 was added into it to make it acidic.Then the solution was converted to a clear saturated brown colour solution. The solution was filtered and clear solution was obtained.Then tri ethanol amine (about 80 ml) was added to it. After this a gel type precipitated substance was produced. Again $HNO_3$was added to it to maintain the pH acidic(between 0-3).Then the solution was heated by Hot plate Method at 200°C and carbonaceous mixture was obtained.Then the mixture was heated again by 650°C to obtain $ZnFe_2O_4$.

Schematic representation of the process is given in fig.1.



(Fig-1)

Below pictures show the preparation of product step by step as mentioned.
Step-1 .The product after mixing of two powders($Fe(NO_3)_3$ and $Zn(CH_3CO_2)_2$) .
Step-2. After complete Mixture.
Step-3. After addition of TEA.
Step-4. After addition of HNO3.
Step-5. Heating Of sample on Hot-Plate.
Step-6. Various Phase Change.
Step-7. After Heating the pure product obtained.
Step-8. After Heating the substance on Container.
Step-9. Powdered form of $ZnFe_2O_4$.

[STEP-1]

[STEP-2]

[STEP-3]

[STEP-4]

[STEP-5]

[STEP-6]

[STEP-7]

[STEP-8]

POWDERED FORM OF ZINC FERRITE

4.1 .CHARACTERIZATION TECHNIQUE:

In order to get exact information about the crystal structure, surface morphology, particle size and optical band gap, the following characterisation instrumentation are used for analysis:

X-ray diffractometer for structural characterization, Scanning electron microscope for surface morphology and particle size distribution, and UV-Visible Spectroscopy for measurement of optical band gap.

4.2 X-ray diffractometer (XRD)

X-ray diffraction technique has been widely used (i) to identify the various phases within materials, (ii) to determine crystal structural and (iii) to estimate crystallite size and lattice parameter of unit cell of the materials. The basic principle lies on the mechanism of electron (X-ray) diffraction within the crystalline lattice . Since all the in a crystalline solid are regularly arranged with interatomic spacing of the order of few angstrom , the crystal can behave as a three –dimensional grating for X-rays. When monochromatic an x-ray beam passes through such crystalline solid , the x-ray electron gets diffracted as the wavelength of X-ray is comparable to interatomic spacing with the solids. IN 1912, W.H Bragg and W.L. Bragg put forward a model which generates the condition for diffraction considering the reflection of X-rays beam from atomic planes as shown in fig.2.13. It was discovered that the constructive diffraction pattern will occur in accordance with Bragg's law condition

$2d\sin\theta = n\lambda$;path difference for n = 1,2,3…….

Where n denotes an integer value , d is the interatomic spacing , λ is the wavelength of monochromatic x-ray beam of incident on the set of parallel planes at a glancing angle θ.

We have used X-ray characterization using copper Cu-Kα radiation having wavelength , $\lambda = 1.5418$ Å for sample characterization. It uses a ceramic tube consists of a tunstten power of the X-ray generator is 3 KW.the resolution of this instrument in terms of scanning angle is 0.001°. the crystalline size (t) is determined from the Scherer's formula : $t = 0.89\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray; β is the full width at half maxima (FWHM measured in radians) and θ is the Bragg's angle. The lattice parameters of the samples have been measured using Wincell XRD software.

4.3 UV-Visible spectroscopy

Ultraviolet-visible spectroscopy refers to the absorption spectroscopy or reflectance spectroscopy in the ultraviolet –visible spectral region. The wavelength range for source used is from 200 nm to 800nm (from UV to visible range). The electronic transition takes place when the incident light beam shines on a sample. In both absorption and reflectance modes, the incident light with a certain wavelength is absorbed by the sample through electronic excitation from the ground state to excited state. At the transition edge, a sharp rise in absorption will occur. The band gap (Eg) of a semiconductor material can be determined by using the formula : Eg = hc/λ where h is the planck's constant , c is the velocity of light and λ is the wavelength of light at where sharp increase in absorption occurs for the given specimen. The optical band gap of the specimen is always measured in terms of electron volt (eV) using the formula : Eg = (1239.8/λ)eV where λ in nm.

[Fig: UV/Vis spectrometer (UV-2600- Shimadzu]

4.4 SCANNING ELECTRON MICROSCOPE-:

The scanning electron microscope uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derived from the electron reveal information about the sample including external morphology (texture), chemical composition and crystalline structure and orientation of materials making up the sample. In most application data are collected over a selected area of the surface of the sample, and a two dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample, the approach is especially useful in qualitatively or semi-qualitatively determining chemical compositions(using EDS), crystalline structure, and crystal orientations(using EBSD).

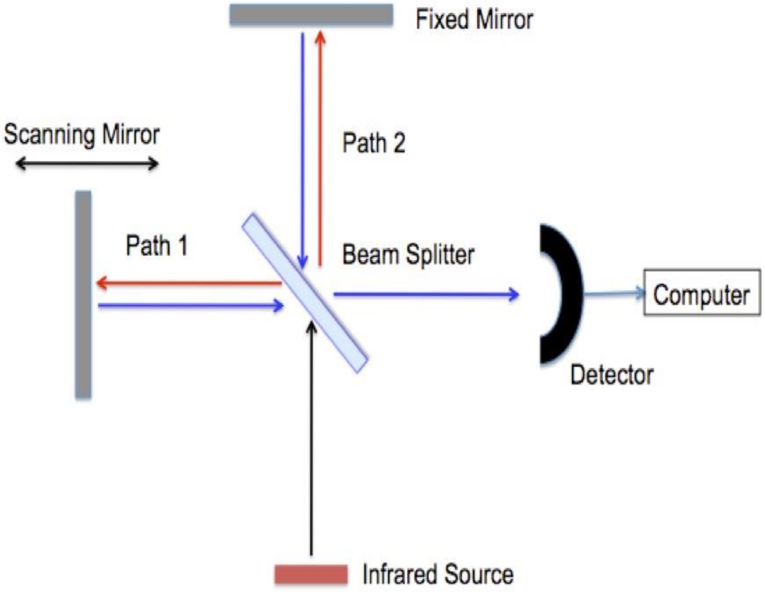
4.5 FTIR (FOURIER-TRANSFORM INFRA-RED SPECTROSCOPY):

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. For chemical analysis IR instrumentation was discovered to be the first analytical technique and has been used since fifty years. Fig 2.6 shows the FTIR spectrometer (Nicolet 1S5 Mid Infrared FTIR spectrophotometer) which was used for analysing the composite films.

Commercial FTIR was invented during 1970 as an advanced IR Spectroscopy in terms of capability and performance. FTIR is technique to detect the chemical bonds present in the sample by the spectrum produced on the absorption of IR radiation. It is considered as fingerprint of molecules. It has some advantages over dispersive IR spectroscopy. In IR Spectroscopy a spectrum is created by the collection of signals of IR at each wave number separately where as in FTIR spectrum over the whole range of wave number is generated simultaneously. Even signal to noise ratio is very less in comparison to IR. Here, in the present study the FTIR is measured at room temperature.

[Fig Nicolet 1S5 Mid Infrared FTIR spectrophotometer]

The samples analysed must not be more than 20micrometre and should not be less than 1micron. Because the excess thick samples can absorb more IR radiation and transmittance cannot be calculated. Similarly, for excess thin samples absorption is too weak to be determined. There are different sampling methods for different samples. Powder samples are mixed with mulling agent and liquid samples are sandwiched in between KBr for characterization process.



[Fig:FTIRspectroscopy]

CHAPTER-5

5.RESULT AND DISCUSSION

5.1. Phase analysis

From the figure 1 show XRD peaks of the crystalline $ZnFe_2O_4$. sol-gel powders after drying at 100°C for 24 hours, which indicates the characteristic peaks corresponding to crystalline $ZnFe_2O_4$. are accurately matched to the three major peaks from JCPDS card number 75-2099. There were no traces of $Zn(CH_3CO_2)_2$ and $Fe(NO_3)_3$ in powder or in calcined $ZnFe_2O_4$. samples. The interesting result is that the crystalline of $ZnFe_2O_4$. gel powders obtained after drying at 100oC for 24 hours. A similar result has been reported for sol-gel derived BaTiO3 powders prepared from the barium alkoxid . Such result indicates that the degree of crystallization of $ZnFe_2O_4$. gel powders is dependent on the mechanisms of hydrolysis and polycondensation reactions of the mixture rather than the calcination temperature of drying powders. The above results clearly indicate that the synthesis of phase pure crystalline $ZnFe_2O_4$ powder after drying can be possible using the equimolar mixture of $Zn(CH_3CO_2)_2$, ethanol and $Fe(NO_3)_3$.

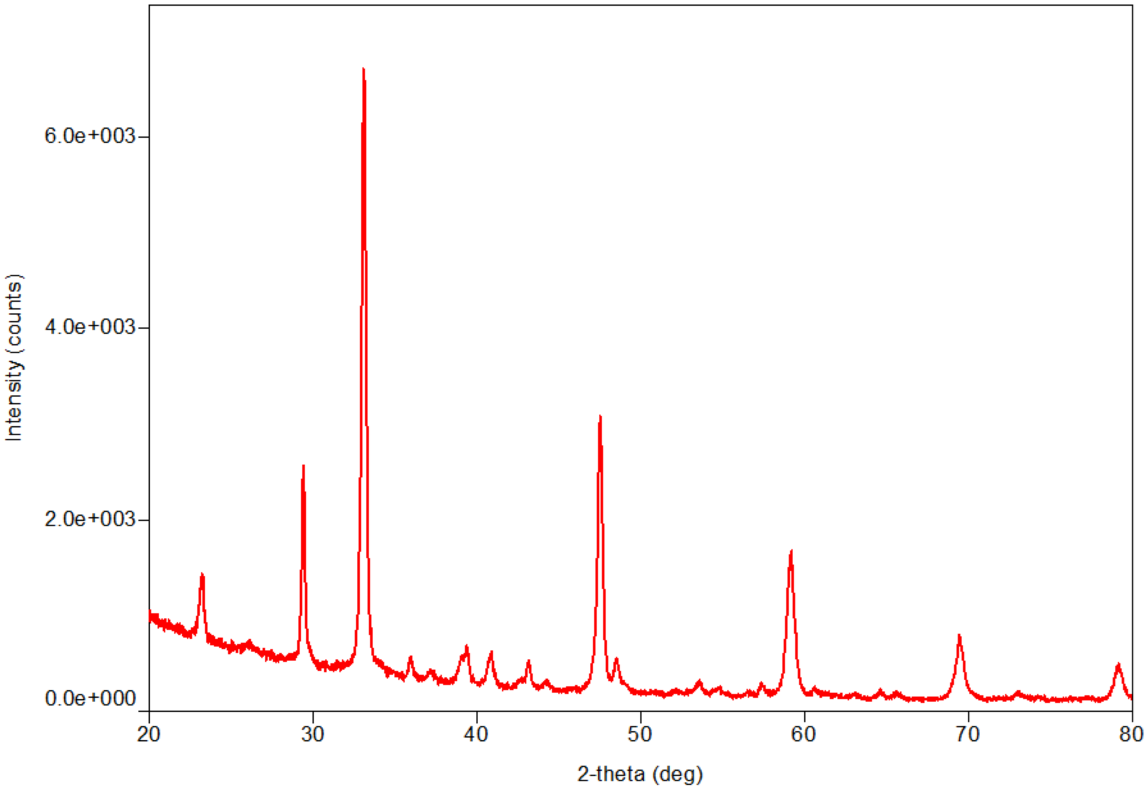
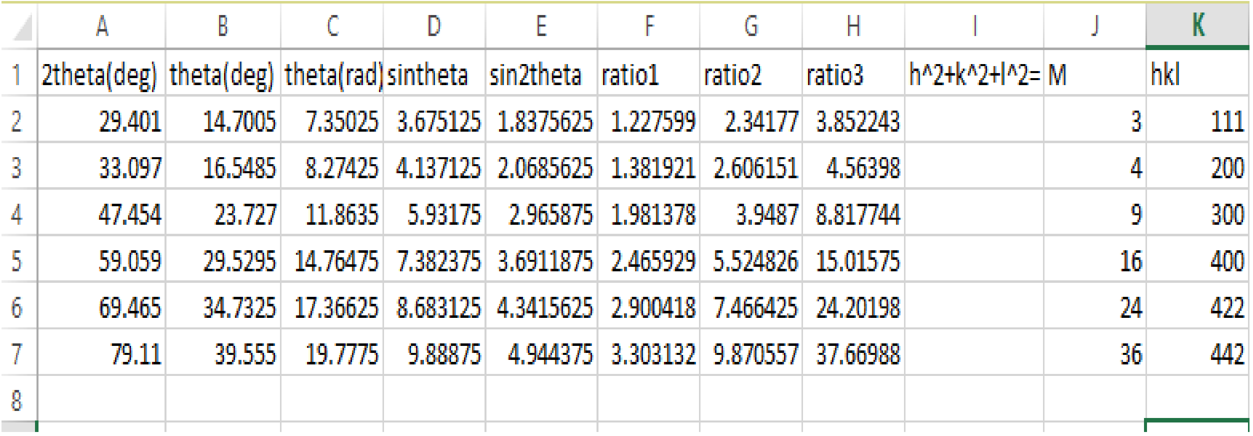


Figure 1. XRD spectrum of $ZnFe_2O_4$ sol-gel powders after drying at 100oC for 24 hours.

Table 1: indexing of Bragg diffraction peaks of $ZnFe_2O_4$

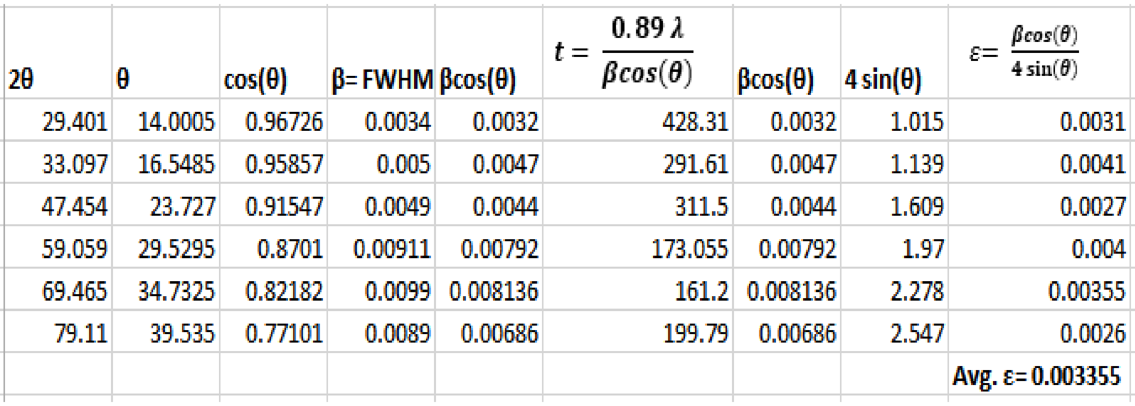


	A	B	C	D	E	F	G	H	I	J	K
1	2theta(deg)	theta(deg)	theta(rad)	sintheta	sin2theta	ratio1	ratio2	ratio3	h^2+k^2+l^2=	M	hkl
2	29.401	14.7005	7.35025	3.675125	1.8375625	1.227599	2.34177	3.852243		3	111
3	33.097	16.5485	8.27425	4.137125	2.0685625	1.381921	2.606151	4.56398		4	200
4	47.454	23.727	11.8635	5.93175	2.965875	1.981378	3.9487	8.817744		9	300
5	59.059	29.5295	14.76475	7.382375	3.6911875	2.465929	5.524826	15.01575		16	400
6	69.465	34.7325	17.36625	8.683125	4.3415625	2.900418	7.466425	24.20198		24	422
7	79.11	39.555	19.7775	9.88875	4.944375	3.303132	9.870557	37.66988		36	442
8											

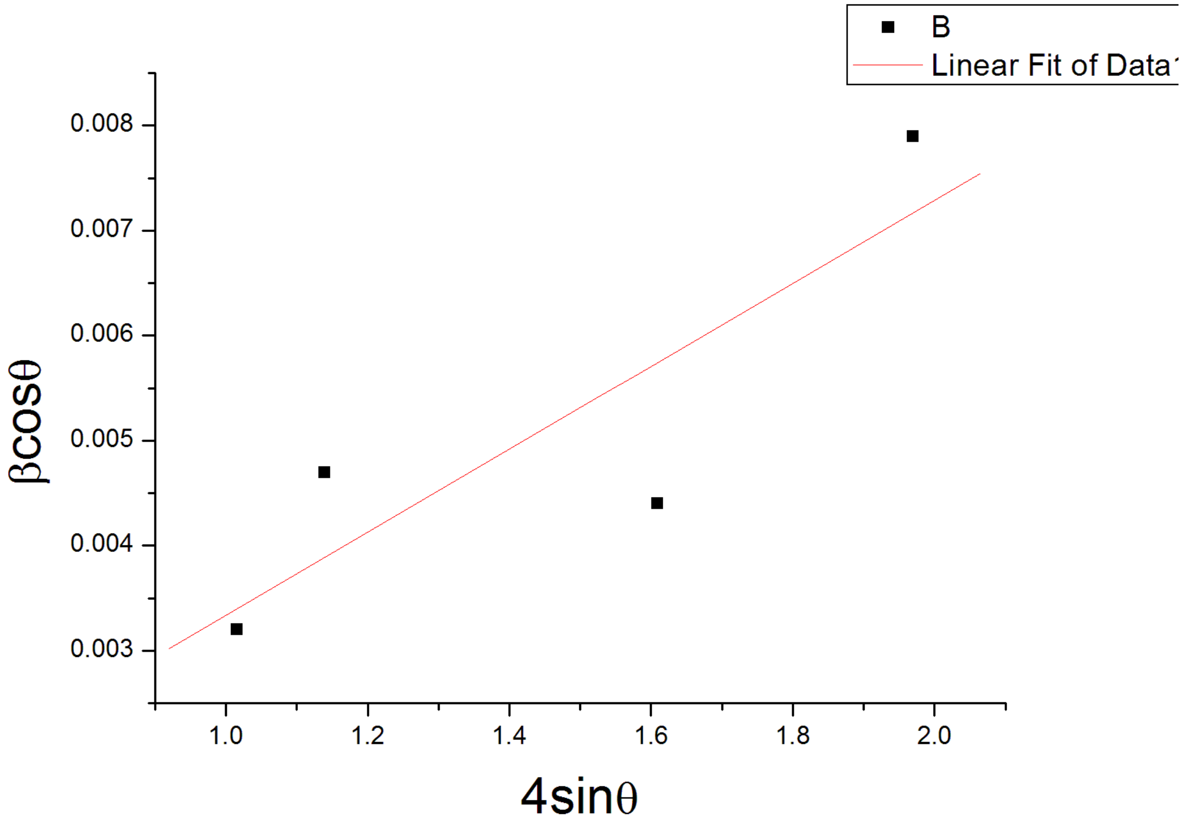
Here the average thickness of the sample $ZnFe_2O_4$ can be calculated by using the schrer Formula. i.e. $t = 0.89\lambda/ \beta\cos\theta$

Here $\lambda = 1.540$Å , β = FWHM(full wave half maximum)

and it is given in the table 2.

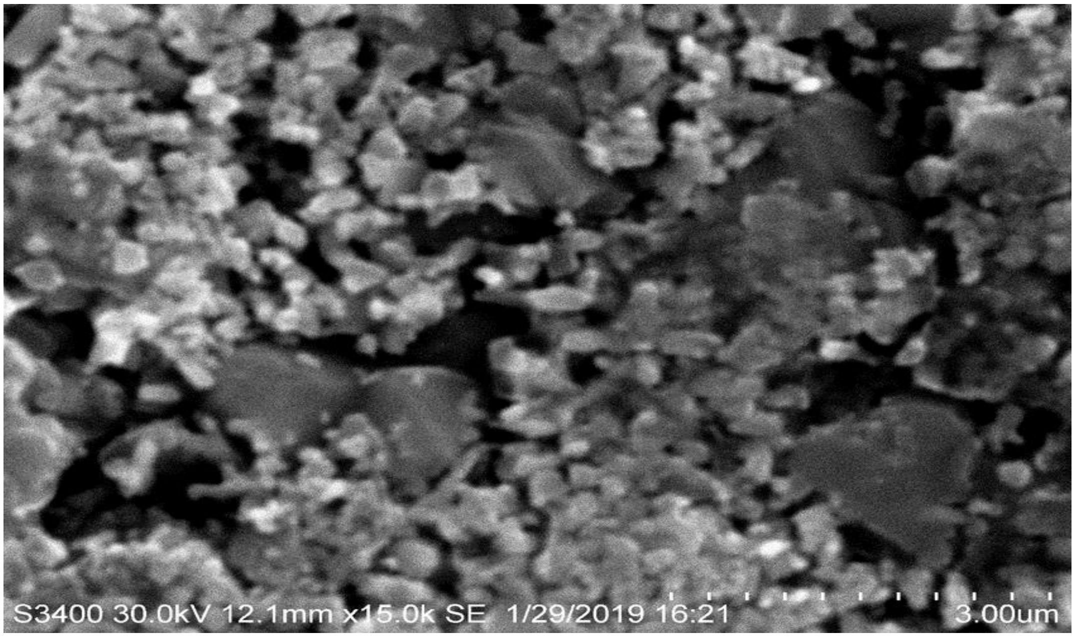


2θ	θ	cos(θ)	β= FWHM	βcos(θ)	$t = \frac{0.89\,\lambda}{\beta cos(\theta)}$	βcos(θ)	4 sin(θ)	$\varepsilon = \frac{\beta cos(\theta)}{4\sin(\theta)}$
29.401	14.0005	0.96726	0.0034	0.0032	428.31	0.0032	1.015	0.0031
33.097	16.5485	0.95857	0.005	0.0047	291.61	0.0047	1.139	0.0041
47.454	23.727	0.91547	0.0049	0.0044	311.5	0.0044	1.609	0.0027
59.059	29.5295	0.8701	0.00911	0.00792	173.055	0.00792	1.97	0.004
69.465	34.7325	0.82182	0.0099	0.008136	161.2	0.008136	2.278	0.00355
79.11	39.535	0.77101	0.0089	0.00686	199.79	0.00686	2.547	0.0026
								Avg. ε= 0.003355

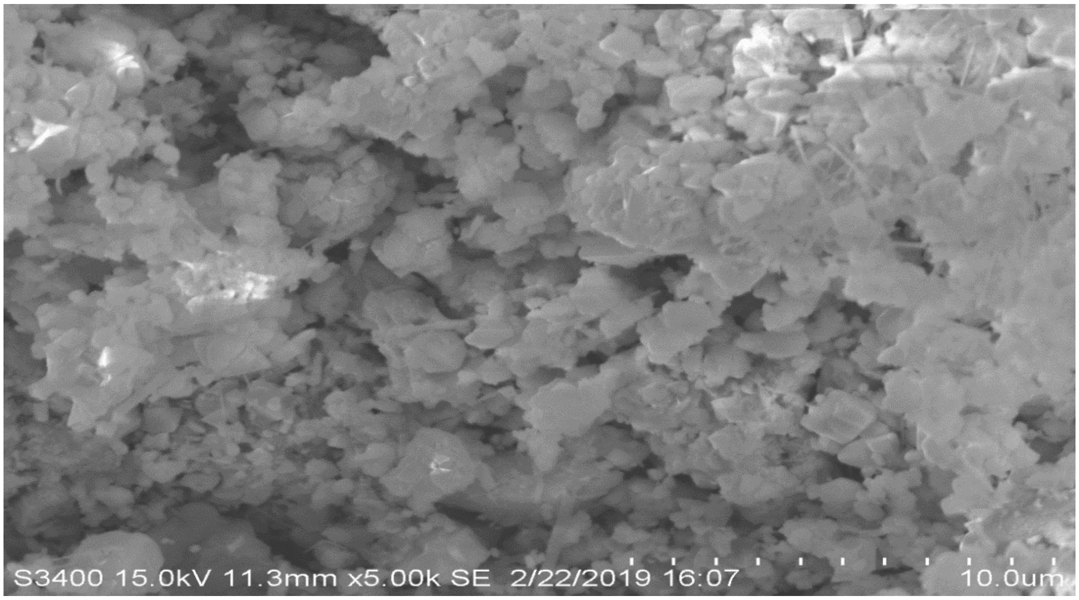


(The dotted graph is done between the 4sinθ and βcosθ.)

The upper two points cannot be taken. Only lower 2 points can be taken to 0btain a graph.



(Fig:a)



(Figb).. scanning electron micrographs of $ZnFe_2O_4$.

The scanning electron micrographs of $ZnFe_2O_4$. are shown in Fig. 2a and 2b, respectively. The sample make cluster and having irregular size. The size varies from 1µm to tens of µm (Fig.2a and 2b). Rod spherical fibre type materials are present in these samples. However, on calcining the particles interact with each other and form a regular shape and size. The average particle size is of order of 10 µm (Fig.2b).

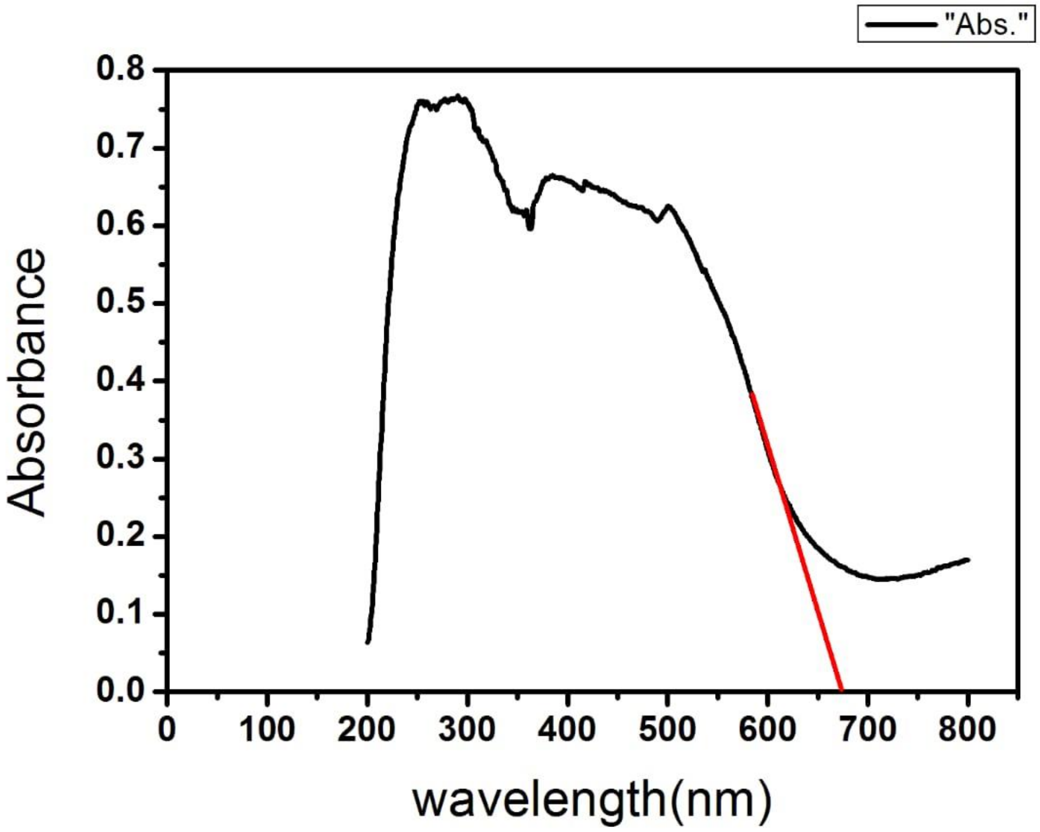


Fig.3. UV-visible spectrum of $ZnFe_2O_4$.

Fig.3. shows the UV-visible spectrum of $ZnFe_2O_4$.. There is a sharp increase in absorbance observed at 257.40 nm wavelength. It is predicted that the band gap othe specimen is at 675.107nm = 4.21eV.

5.2 FTIR analysis

The FTIR data support the for-mation of spinel phase octahedral and tetrahedral site. It was found from HR-SEM image that the synthesized nanoparticles were spherical in shape .In order to study the vibrational properties of ferrite we first review the Group Theory Analysis (GTA) of vibrations for $ZnFe_2O_4$. bulk structures $ZnFe_2O_4$.at room temperature has a tunnel-like structure in a monoclinic symmetry (space group C2/m) with two formulas per unit cell (Z = 2) . Group theory predicts that $_3$ should exhibit 60 vibrational modes distributed as follows: 12 Ag + 18 Au + 12 Bg + 18 Bu . Where Ag (Au) and Bg (Bu) are Raman (IR) active representations. Before analysing the present vibrational study, we should mention that these materials have a tunnel-like structure and it is not appropriate to apply standard factor group analysis, because there is no radial symmetry. Therefore, the analysis will consider the atomic vibrations without specifying the mode symmetry.

FTIR spectra for pure, $ZnFe_2O_4$ have been studied in the region of 400-4000 cm-1 at room temperature (RT) and depicted in the figure . It has been observed from these figures that all samples (pure and doped) exhibited quite similar peaks confirming the formation of pure phase of zinc and iron($ZnFe_2O_4$) samples. All peaks obtained for prepared samples agree well with the previously reported data . Absorption bands around 3430.4cm-1 and 527.69cm-1 for all samples . Pure and doped zinc ferrite prepared in this work using solid state reaction route contain only zinc ferrite as detectable phase with no other significant impurity peak is observed (also confirmed from XRD pattern given in chapter 4 and 5). The peaks were also observed at 3430.4cm-1 , 2340.83 cm-1 , 2166.99 cm-1 , 2105.2cm-1,2016.19cm-1,1408.81cm-1, 1477.31cm-1, 527.69cm-1 . These peaks are quite similar to those reported by Bamberger [33] using Raman spectroscopy for zinc ferrite.

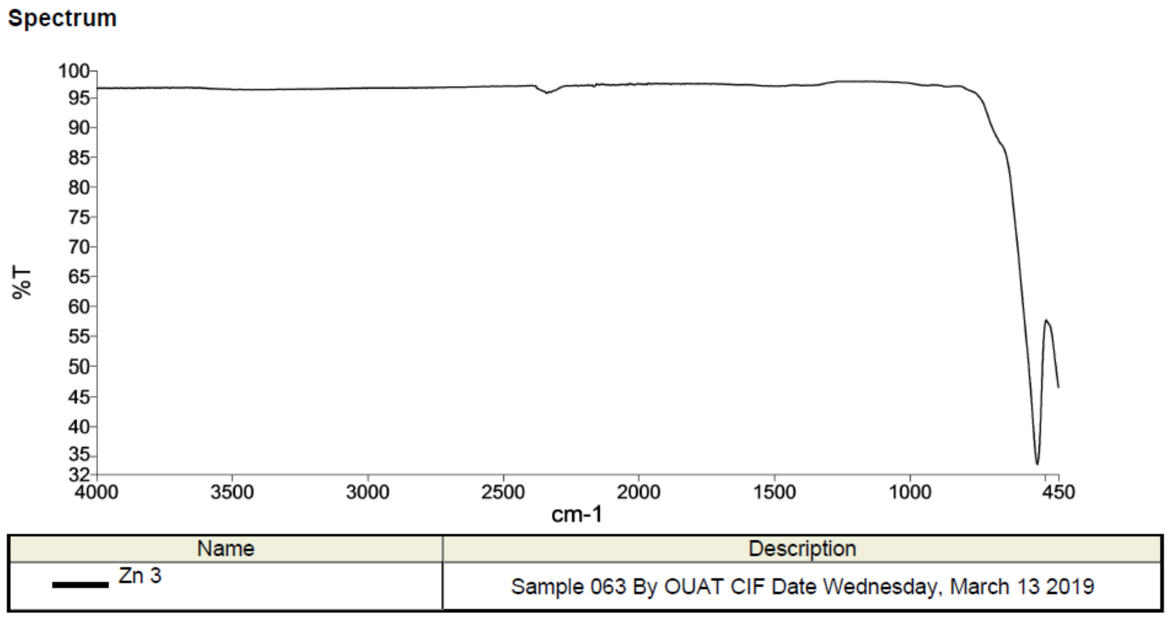


Fig.1.spectrum

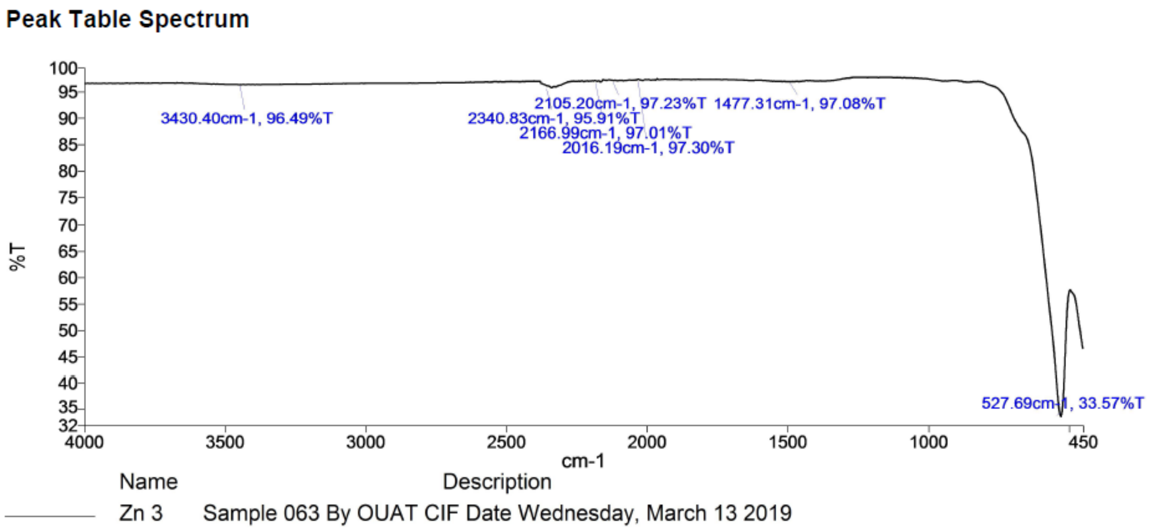
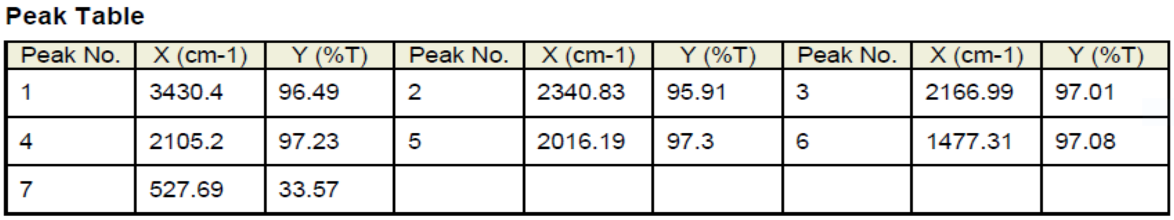


Fig.2. Result spectrum



Peak Table

Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)	Peak No.	X (cm-1)	Y (%T)
1	3430.4	96.49	2	2340.83	95.91	3	2166.99	97.01
4	2105.2	97.23	5	2016.19	97.3	6	1477.31	97.08
7	527.69	33.57						

Using this FITR we can find several peak points of the spectrum

CHAPTER-6

6. Conclusion

From this research work, it can be concluded that pure Zinc Ferrite($ZnFe_2O_4$) nanoparticles can be successfully synthesized by chemical route with low cost. The synthesized zinc ferrite is orthorhombic. It is observed from the scanning electron micrographs that samples have regular shape and size. The heat treatment proves the opportunity to the smaller crystallites to interact with each other and grows in to bigger crystallite and bigger grains. The optical band gap of the specimen is found to be 4.21 eV.

6.1 Recommendation

With the advancement of science and technology, more research should be carried out in the characterization of nano zinc ferrite and other nano materials, to help in identifying and determining more of their properties, because the structure of a compound determines its properties. Also, more work should be carried out on the spinel due to their importance in green chemistry, electronics, solar energy, biomedical e.t.c.

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