Synthesis Of Mn-Zn Ferrites By Combustion Method

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M.Sc. in Physics

by

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Physics Discipline

Goa University

May 2024

Examined by:

Seal of the School

DECLERATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "**Synthesis of Mn-Zn Ferrites by Combustion Method**" is based on the results of investigations carried out by me in the Physics Discipline at the School of Physical and Applied Sciences, Goa University under the Supervision of Dr. Pranav P. Naik. and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will be not be responsible for the correctness of observations / experimental or other findings given the dissertation.

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Name: Mr. Satyawan Kamlakant Shinde

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Date: 08/05/2024

Place: Goa University

COMPLETION CERTIFICATE

This is to certify that the dissertation report "**Synthesis of Mn-Zn Ferrites by Combustion Method**" is a bonafide work carried out by Mr. Satyawan Kamlakant Shinde under my supervision in partial fulfilment of the requirements for the award of the degree of M.Sc. in Physics at the School of Physical and Applied Sciences, Goa University.

8/5/2024

Supervisor: Dr. Pranav Naik

Date: 8/5/2024

Dean: Prof. Dr. Ramesh Pai.

Date: 8/5/2024

Place: Goa University

School of Physical and Applied Sciences
Goa University

ACKNOWLEDGEMENT

I am pleased to present the report of my project work undertaken during my final year in M.Sc. Physics. Although I have worked hard for the success of this project, it would not have been possible without the help and guidance of some people. Therefore, I would like to express my sincere gratitude to those individuals.

First and foremost, I extend my sincerest gratitude to my project guide, Dr. Pranav P. Naik, whose exceptional guidance, encouragement, intelligence, and profound insights were instrumental throughout the project. Sir, your unwavering motivation and inspiration propelled me forward, and I am immensely grateful for your mentorship. Additionally, I express my heartfelt appreciation to Ms. Sugania Chandavelou for her consistent assistance and support throughout the duration of the project. Her guidance and encouragement significantly contributed to its successful completion. Also, I would like to express my heartfelt gratitude towards the esteemed faculty members of the Department of Physics (SPAS) at Goa University for their continuous. I would like to thank the School of Physics and Applied Sciences for providing me with all the required instruments and material for my project work.

I extend my heartfelt gratitude to the dedicated PhD students in the Physics department whose invaluable assistance has significantly contributed to my understanding of various instruments and software. I am also grateful to my family and friends for their unwavering support and encouragement throughout my studies.

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ABSTRACT

Nanocrystalline manganese zinc ferrite powders with chemical composition $Mn_{1-x}Zn_xFe_2O_4$ were prepared using the combustion method. The X-ray diffraction (XRD) technique was used to confirm the phase formation. The XRD pattern indicated the presence of a cubic spinel phase having Fd-3m space group with the crystallite size ranging between 14 and 17 nm. Structural parameters such as lattice constant and crystalline size appreciable dependence on varying zinc concentrations in the ferrite material. Raman spectra confirmed the spinel phase of the ferrite nanoparticles having tetrahedral and octahedral sites The surface morphology of nano powders was analysed using a scanning electron microscope (SEM). The variation of electrical properties such as dielectric constant was also studied and were seen to be administered by cationic distribution at the tetrahedral and the octahedral sites in the spinel structure

Chapter 1

introduction

Identification of problem

There is rapid development of modern industry that brings about various toxic, harmful, flammable and explosive gases such as volatile organic compounds and hydrogen sulphides, which is dangerous to environmental safety and human health. Therefore, gas analysis, detection are of great concern to the industry. The conventional gas analysis methods such as high-performance liquid chromatography, spectrometry-gas chromatography can detect gases accurately. but due to the complexity of the procedures, they are both time-consuming and expensive. As a result, the gas sensors that can be easily manufactured and and can work at room temperature and less costs have attracted great interests from both industry . A stream of studies has shown that metal oxide semiconductor (MO) sensors are considered to be effective solutions to detection of harmful gases, because of their high sensitivity, fast response and easy availability. The MO gas sensing materials can be divided into two categories based on a number of types of metal oxides involved in the material: single and composite metal oxides. Single metal oxides have been widely studied as gas sensing materials. These include zinc oxide, tin oxide, tungsten oxide, titanium oxide and iron oxide. The high-performance gas sensors based on single metal oxides possess the characteristics of easy integration and good repeatability, and can effectively detect a variety of gases (CO, NH_3, O_3, etc.). However, the selectivity and recovery property of single-phase gas sensing materials for reducing gases such as volatile organic compounds still need to be enhanced. In this regard, attempts were made to modify single metal oxides morphology by

doping of noble metal catalysts or the combination with other materials, resulting in enhanced sensing properties.

Why we use thin films

Spinel ferrites have recently attracted considerable research interest on their structural, magnetic and electrical properties . They are used in microwave devices, integrated circuits, reading/ writing heads, sensors and catalytic material beacause of their great magnetic permeability and dielectric constant, low dielectric loss at low frequencies. With the development of high-frequency and magnetic and magneto-optical memory devices of nano-structured materials having small dimensions, there has been a significant increase in the interest in ferrite thin films in recent years. There are many applications of ferrite thin films, such as gas or humidity sensors for which low density and nano-sized materials are required . Properties of ferrite thin films are often found to be different from that of the bulk for various reasons such as crystallite size, high defect density, grain boundaries, texture, depend very much on synthesis methods.

Problem faced during synthesising thin films

The most important problems faced by researchers how to fabricate ferrite films using a simple technology with low temperature heat treatment and low vacuum. To achieve potential applications, ferrite films have been fabricated earlier using various methods viz. RF sputtering , plasma laser deposition etc. These methods usually involve elaborate and costly apparatus and complicated process. Furthermore, the high deposition

temperature limits the option of the substrate material as well as restricts different applications of ferrite thin films , nanomaterials play a crucial role in thin film fabrication due to their unique properties and functionalities. Here's a breakdown of some commonly used nanomaterials in thin film technology:

Namomaterials

Nanoparticles: These are particles with dimensions ranging from 1 to 100 nanometers. Nanoparticles can be made from various materials such as metals (like gold, silver, and platinum), metal oxides (like titanium dioxide and zinc oxide), and semiconductors (like silicon). They are widely used in thin film fabrication for applications such as solar cells, sensors etc. Nanoparticles offer high surface area-to-volume ratios, tunable optical and electronic properties, and enhanced porosity.

Nanowires: Nanowires are elongated nanostructures with diameters on the order of nanometers. They can be made from materials like silicon, zinc oxide, and gallium arsenide. Nanowires are used in thin films for various purposes, including electronics ,photonics and energy storage (like batteries and supercapacitors).

Nanosheets: Nanosheets are two-dimensional nanomaterials with thicknesses typically ranging from one to a few atomic layers. Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, is one of the most well-known nanosheets.. Nanosheets are used in thin film fabrication for applications such as flexible electronics and coatings. They exhibit exceptional mechanical strength, high surface

area, and unique electronic properties. Each type of nanomaterial offers distinct advantages and can be designe to meet specific requirements in thin film fabrication.

Properties that make namomaterial suitable for thin film synthesysis

Nanomaterials possess several unique properties at the nanoscale that make them highly suitable for thin film applications:

High Surface Area: Nanomaterials have a significantly higher surface area-to-volume ratio compared to bulk materials. This increased surface area provides more active sites for interactions with other materials, such as gases in sensors or electrolytes in batteries. In thin film applications, high surface area enhances surface reactivity, catalytic activity, and adsorption/desorption processes, leading to improved performance in various devices.

Improved Electrical Conductivity: Certain nanomaterials possess superior electrical conductivity compared to their bulk counterparts. For example, silver nanoparticles exhibit excellent electrical conductivity, while carbon-based nanomaterials like graphene demonstrate high electrical conductivity. Incorporating these nanomaterials into thin films can enhance heat dissipation, electrical conductivity, and overall device performance in electronics and energy storage devices.These unique properties of nanomaterials at the nanoscale make them highly attractive for thin film applications, enabling the development of advanced and multifunctional materials for various technological domains.

Application of thin films

Nanomaterial-based thin films have revolutionized sensor technology by offering unique properties that enable sensitive, selective, and versatile sensing platforms.

Gas Sensors:

Nanomaterials: Metal oxides (e.g., tin dioxide), zinc oxide carbon nanotubes graphene, and metal nanoparticles (e.g., gold nanoparticles).Mechanism: Gas sensors typically operate based on changes in electrical conductivity, capacitance, or optical properties induced by gas adsorption or reaction on the sensor surface. Nanomaterials enhance sensitivity due to their high surface area and unique electronic properties. Advancements: Recent advancements in gas sensors include improved sensitivity and selectivity achieved through the functionalization of nanomaterials with specific receptors or dopants, as well as the integration of nanomaterials into flexible and wearable sensor platforms

-

Biosensors:

Nanomaterials: Quantum dots, gold nanoparticles, carbon nanotubes, graphene oxide, and nanowires.Mechanism: Biosensors detect biological molecules (such as proteins, DNA, and enzymes) by transducing biochemical interactions into

measurable signals, such as electrical, optical, or mass changes. Nanomaterials enhance sensitivity and enable label-free detection through amplified signal transduction and improved biomolecule immobilization. the development of multiplexed detection platforms enabled by nanomaterials, as well as the integration of miniaturized and portable biosensing devices for point-of-care diagnostics and personalized healthcare.

Chemical Sensors:

Nanomaterials: Metal-organic frameworks (MOFs), functionalized carbon nanotubes, graphene, and porous silicon.Mechanism: Chemical sensors detect specific analytes by interacting with them through chemical reactions, adsorption, or absorption processes. Nanomaterials provide high surface area, tunable pore structures, and tailored surface chemistry, leading to enhanced sensitivity and selectivity the development of nanomaterial-based sensor arrays for simultaneous detection of multiple analytes, as well as the integration of nanomaterials into wearable and implantable sensor platforms for continuous monitoring of environmental and biological markers.

Optical Sensors:

Nanomaterials: Plasmonic nanoparticles (e.g., gold and silver nanoparticles), quantum dots, and photonic crystals.Mechanism: Optical sensors detect changes in light intensity, wavelength, or phase caused by interactions between nanomaterials and analytes. Nanomaterials offer tunable optical properties, localized surface plasmon

resonance (LSPR), and enhanced light-matter interactions, enabling ultrasensitive detection and real-time monitoring. the development of nanomaterial-based surface-enhanced Raman scattering platforms for trace-level detection, as well as the integration of nanomaterials into chip and smartphone based sensing devices for onsite and remote sensing applications.

Overall, nanomaterial-based thin films have propelled sensor technology to new heights by enabling higher levels of sensitivity, selectivity. Ongoing research efforts continue to push the boundaries of nanomaterial-based sensor technologies, paving the way for innovative solutions to address pressing societal challenges in healthcare, environmental monitoring, and beyond.

What are ferrites ?

Ferrite are ceramic-like material having different properties, which are useful in several types of application. These are composed of iron oxide and other metals in the chemical combination.

Several ferrites adopt the spinel structure having the formula AB_2O_4, where A and B indicate different metal cations, usually including iron (Fe).

Spinel ferrites are characterized by a formula MFe_2O_4

M stands for divalent metal ions such as Cu, Ni, Mg, Mn, Co, Zn, Cd, etc

A ferrite is a ceramic material that is made up of iron oxide (Fe2O4) in large proportion mixed with metallic element such, manganese (Mn), nickel (Ni), zinc (Zn) in small proportions. The nature of both the iron oxide and the metal is electrically non-conducting

and ferrimagnetic. Ferrimagnetic material is one that possesses unequal opposing magnetic moments which allow such materials to retain spontaneous magnetization. Ferrites are generally classified into two types: hard ferrites and soft ferrites . Hard ferrites have high coercivity and such materials are difficult to magnetize. Therefore these materials are used in making permanent magnets which are used for applications in refrigerator, loudspeaker, washing machine, TV, communication systems, switch mode power supplies, dc-dc converters, microwave absorbing systems, high frequency applications, refrigerator, loudspeaker etc. . On the other hand, soft ferrites have low coercivity as a result of which their magnetization can easily be altered. Soft ferries are good conductors of magnetic field which has led to its wide range of applications in electronic industry such as developing transformer cores, high frequency inductors and as microwave components.

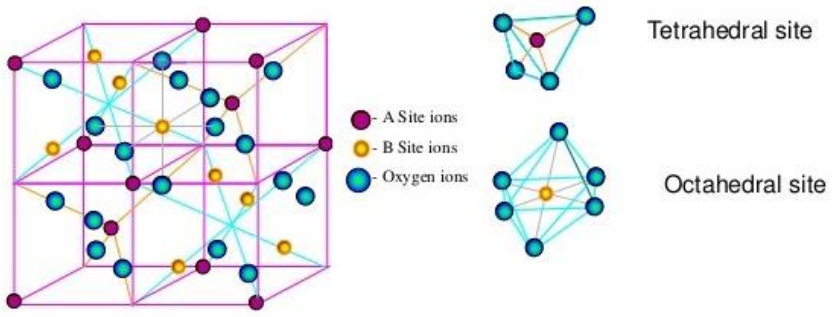


Figure 1 : Spinel ferrite

Types of ferrites

1.**Normal spinel ferrites**

A ferrite is called normal spinel when the divalent metal ions occupy the tetrahedral (A) sites while Fe^{3+} ions are at octahedral (B) sites

example, zinc ferrite ($ZnFe_2O_4$)

2.**Inverse spinel ferrites**

In inverse spinel ferrite, tetrahedral (A) site contains one trivalent ferric ion Fe^{3+} while (B) site contains remaining trivalent ferric ions Fe^{3+} and the divalent metallic ions M^{2+}

($CoFe_2O_4$, and $NiFe_2O_4$

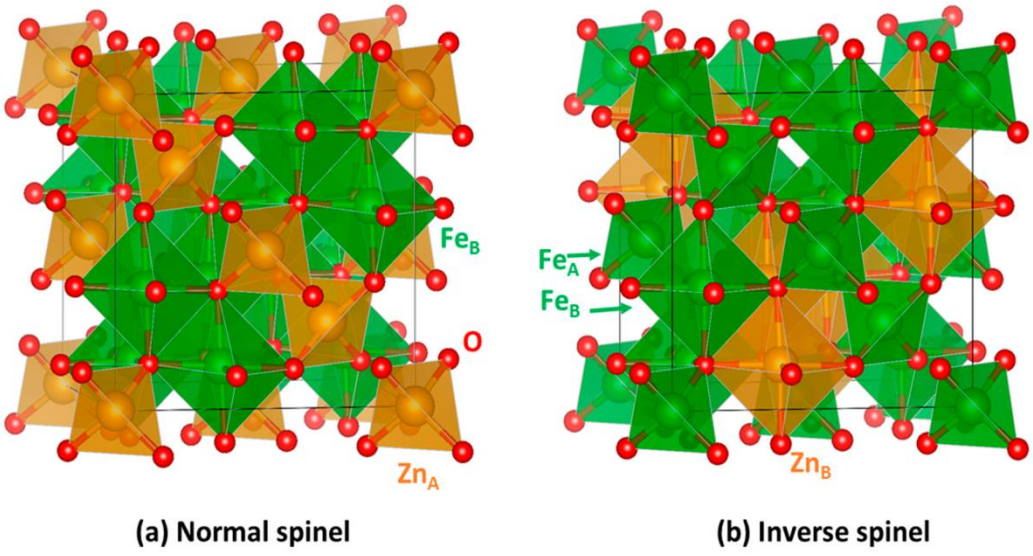


Figure 2 : types of ferrite

Classification of ferrites

In the classification of ferrites, two main criteria, i.e., crystal structure and magnetic properties. The magnetic properties of ferrites are the consequences of electronic configuration and mutual interactions of the ions present in it. So the study of crystal structure is essential to understand basic properties of these materials. According to crystal structure, ferrites are classified into four groups; spinel (cubic), hexagonal, garnet, and orthoferrites , while according to magnetic properties, they are soft and hard ferrites .

Main objective

Our main aim is the Preparation of $Mn_{1-x}Zn_xFe_2O_4$ and different composites by incorporating Mn in Zn ferrite

By varing the different concentration of Mn and Zn powder

The concentration are as follows :

1) $MnFe_2O_4$

2) $Mn_{0.8}Zn_{0.2}Fe_2O_4$

3) $Mn_{0.6}Zn_{0.4}Fe_2O_4$

4) $Mn_{0.4}Zn_{0.6}Fe_2O_4$

5) $Mn_{0.2}Zn_{0.8}Fe_2O_4$

6) $ZnFe_2O_4$

Chapter 2

Literture servey

- Paper : **Growth of zinc ferrite aligned nanorods for liquefied petroleum gas sensing**
- Auther : *Satyendra Singh a,1 , Archana Singh b , R.R. Yadav a , Poonam Tandon*
- In this zinc ferrite thin film sensor synthesised using sol gel method
- Zinc ferrite prepared have two different types of surface morphologies (mixed shaped nanorods and vertically aligned nanorods).
- The LPG sensing properties of the vertically aligned assembled nanorods are found improved significantly in comparison to mixed shaped nanorods.
- zinc ferrites thin films sensor performance was found to be better than that of others.

Thus the zinc ferrite proved to be good at the fabrication of LPG sensor operable at room temperature

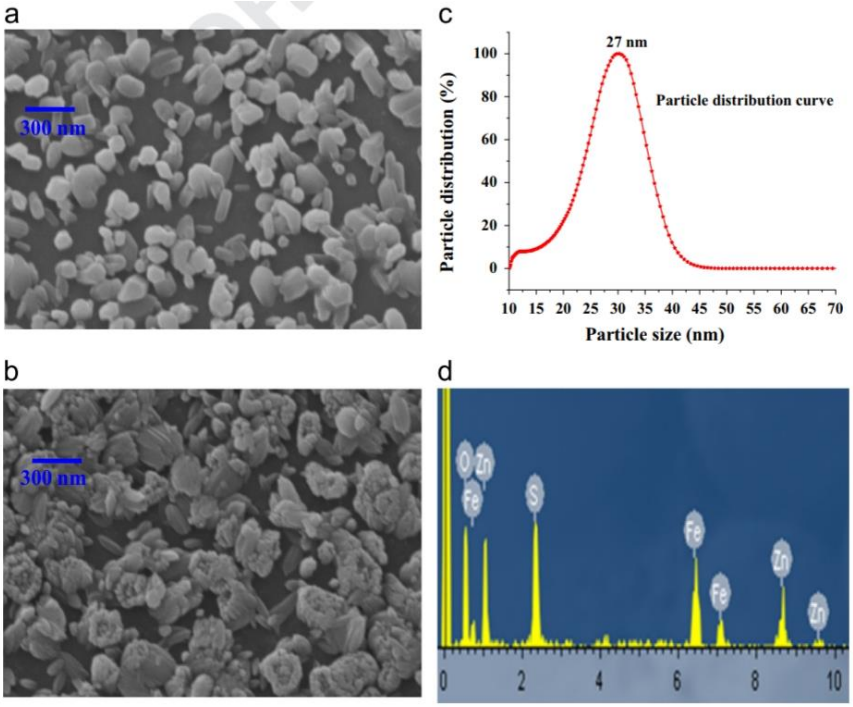
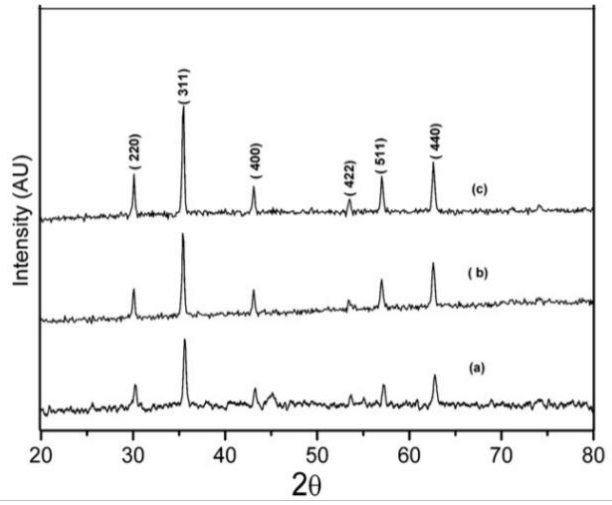


Fig. 1. SEM image of: (a) G-1 and (b) G-2, (c) particle size distribution curve, (d) EDAX of G-2.

Paper : **Combustion synthesis of magnesium ferrite as liquid petroleum gas (LPG) sensor: Effect of sintering temperature**

- **Auther :J.Y. Patil a , M.S. Khandekar a , I.S. Mulla b , S.S. Suryavanshi a,***
- Magnesium ferrite (MgFe2O4) was synthesis using combustion method with glycine as a fuel and their application as a gas sensor was studied
- The structural and surface morphological properties were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively
- The XRD shows single phase spinel type structure



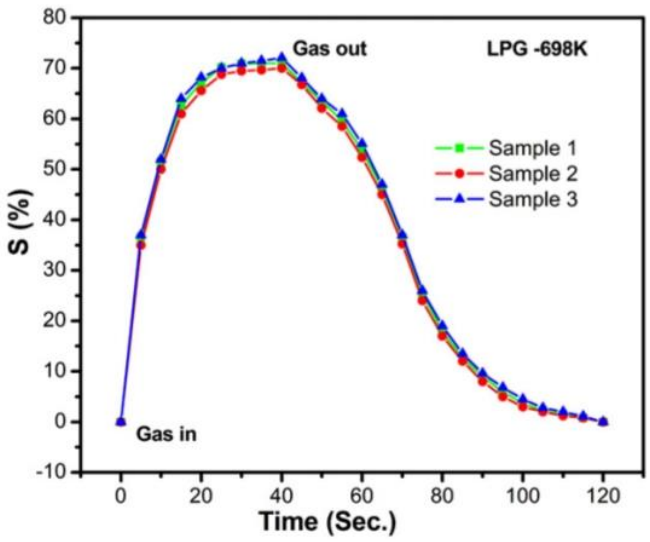


Fig. 8. The dynamic response transients of different samples of G2 toward LPG.

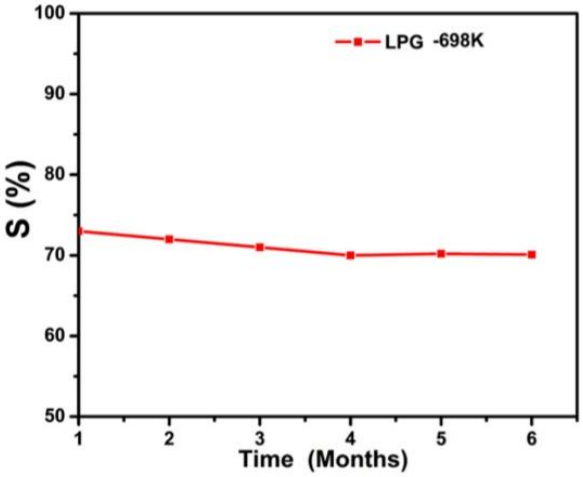
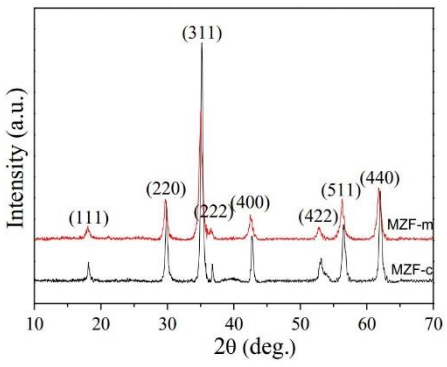


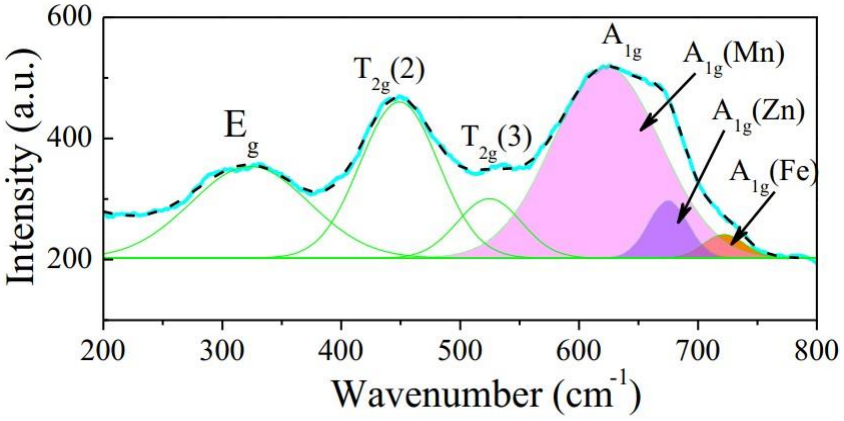
Fig. 9. The LPG sensing stability studies for G2 at an operating temperature of 698

Paper: Synthesis and Characterization of MnZn Ferrite Nanoparticles with Improved Saturation Magnetization

Author: Haiyan Fang and et al.

- $Mn_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles with improved saturation magnetization were prepared by a modified hydrothermal method.
- This method involves a chemical co-precipitation of hydroxides under a vacuum condition using potassium hydroxide as a precipitating agent, followed by a separate hydrothermal process
- XPS results show that the Mn cations of the nanoparticles prepared by modified hydrothermal method have lower average valence.
- The Mn Zn ferrite nanoparticles prepared by modified hydrothermal method have smaller diameter (16.1 nm, calculated by XRD) and higher room temperature saturation magnetization, 80 emu/g, which is even better than the reported value.
- The saturation magnetization of the particles prepared by modified hydrothermal method is 1.6 times of the particles prepared by conventional hydrothermal method

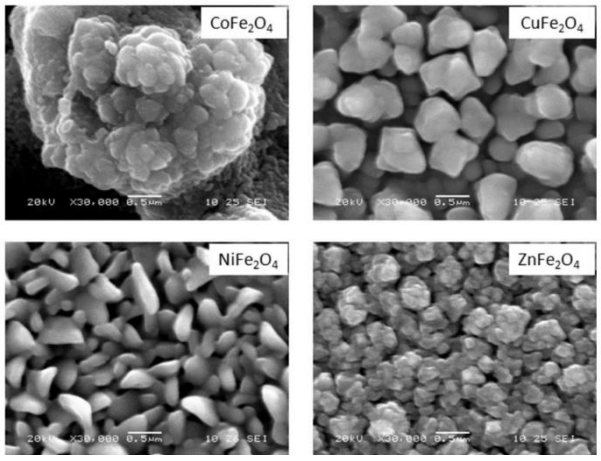


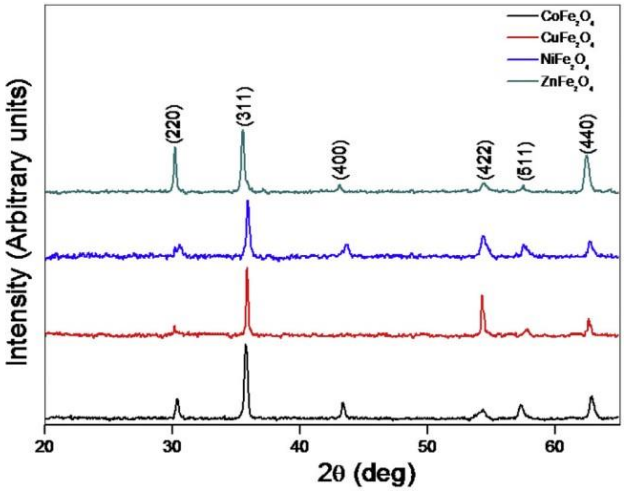


Paper : Ferrite thin films: Synthesis, characterization and gas sensing properties towards LPG

Auther: Pratibha Rao , et al

- Nanocrystalline (Co, Cu, Ni, Zn) ferrite thin films have been deposited onto the Si (100) and alumina substrates by spray pyrolysis deposition technique.
- The structural properties of (Co, Cu, Ni, Zn) ferrite thin films were investigated by X-ray diffraction (XRD) technique which confirms polycrystalline nature and single phase spinel structure.
- The surface morphology was studied using scanning electron microscopy (SEM) which reveals spherical morphology for these films except $NiFe_2O_4$ films that exhibit petal like structure.
- The optical transmittance and reflectance measurements were recorded using a double beam spectrophotometer. The optical studies reveal that the transition is direct band gap energy.
- The VSM analyzes reveal the predominant ferrimagnetic nature for $CuFe_2O_4$ films. The gas sensing properties towards Liquid Petroleum Gas (LPG) revealed that $ZnFe_2O_4$ films are sensitive at lower temperature while $NiFe_2O_4$ films show steep rise at higher temperature.

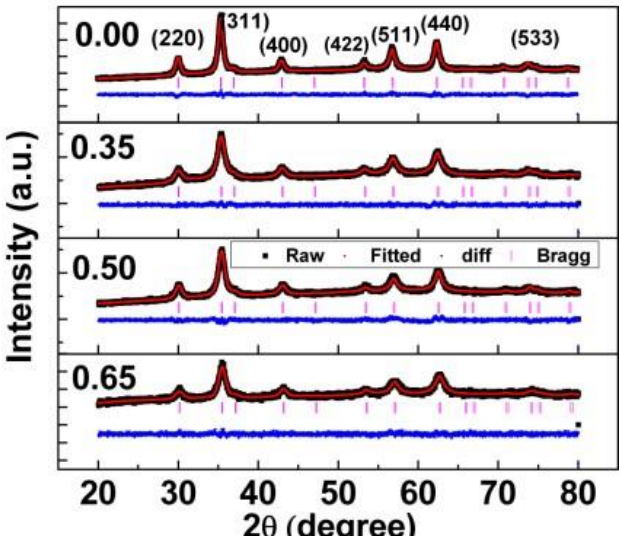


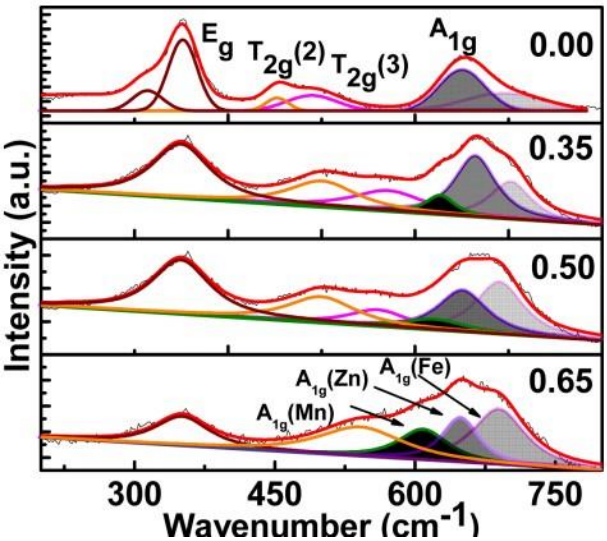


Paper: Micro Raman, Mossbauer and magnetic studies of manganese substituted zinc ferrite nanoparticles: Role of Mn

Author: Suneetha Thota, Subhash C. Kashyap, Shiv K. Sharma, V.R. Reddy

- A series of Mn-Zn Ferrite nanoparticles (< 15 nm) with formula $Mn_xZn_{1-x}Fe_2O_4$ (where x = 0.00, 0.35, 0.50, 0.65) were successfully prepared by citrate-gel method at low temperature (400 °C).
- X-ray diffraction analysis confirmed the formation of single cubic spinel phase in these nanoparticles.
- The FESEM and TEM micrographs revealed the nanoparticles to be nearly spherical in shape and of fairly uniform size.
- The fractions of Mn^{2+}, Zn^{2+} and Fe^{3+} cations occupying tetrahedral sites along with Fe occupying octahedral sites within the unit cell of different ferrite samples are estimated by room temperature micro-Raman spectroscopy.
- Low temperature Mossbauer measurement on $Mn_{0.5}Zn_{0.5}Fe_2O_4$ has reconfirmed the mixed spinel phase of these nanoparticles.
- The optimized substitution of manganese for zinc 2 improves the magnetic properties and makes these nanoparticles a potential candidate for their applications in microwave region and biomedical field.

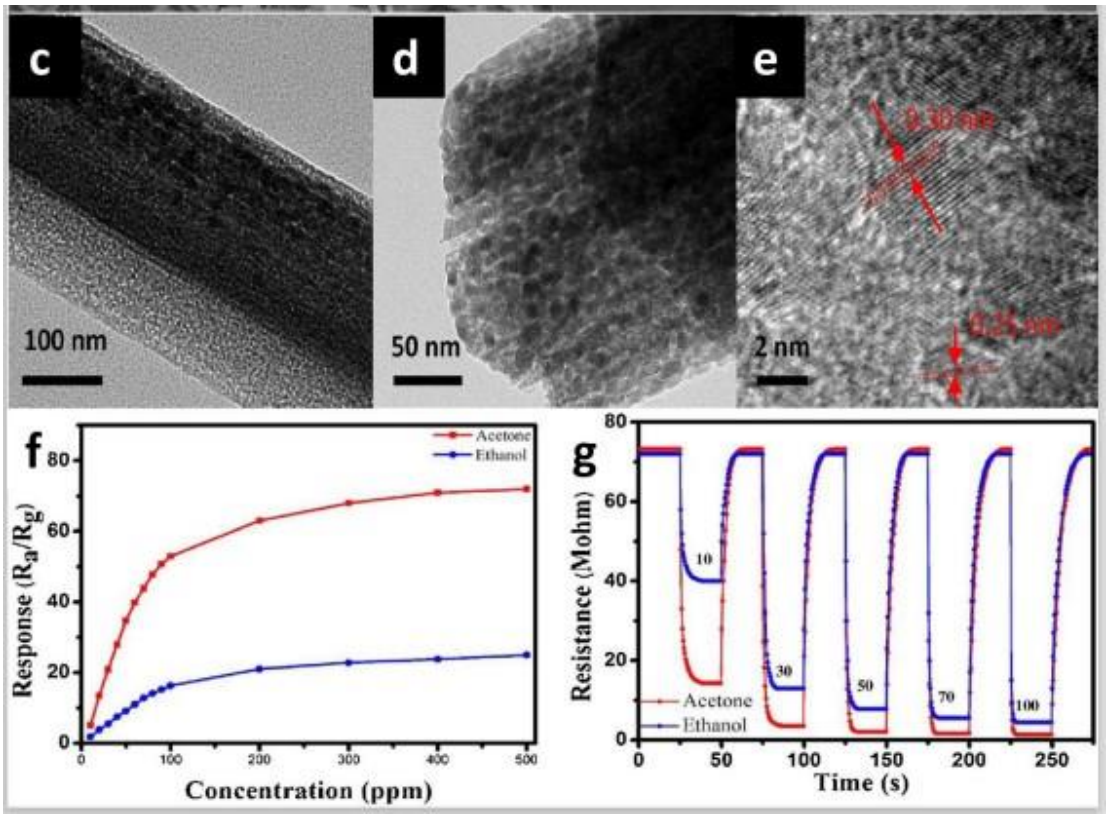




Paper: Zinc Ferrite Based Gas Sensors: A Review

Author: Kaidi Wu et al

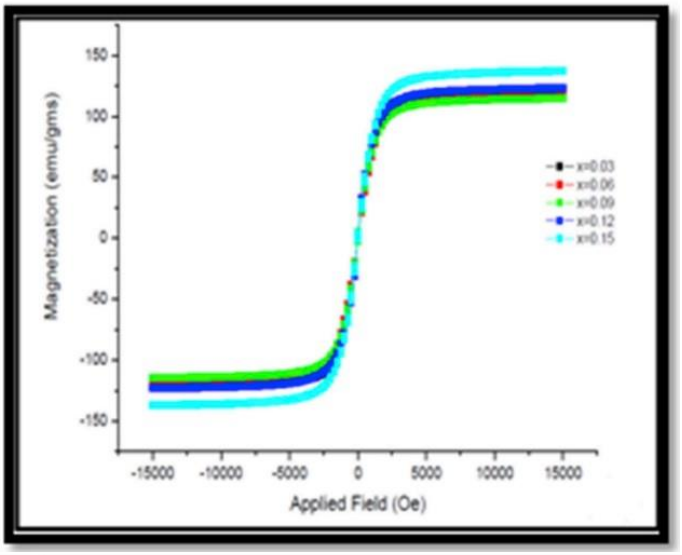
- In this article, the research progress in ZnFe2O4 based gas sensors was reviewed from three aspects: nanostructure, element doping and heterostructure.
- The metal element doping of ZnFe2O4 improves the specific surface area on the basis of preserving the original crystal structure and offers the activation energy.
- As for the composite, the heterojunction is formed at the interface between different materials, and the response of sensor is adjusted mainly through the function of the formed electron depletion layer. By comparison, it can be found that improving the microstructure, proper metal element doping or material compounding can improve sensing performance of ZnFe2O4 based gas sensors to a certain extent.
- To realize stable room temperature or low-temperature detection and rapid recovery of such sensors, new research directions are needed



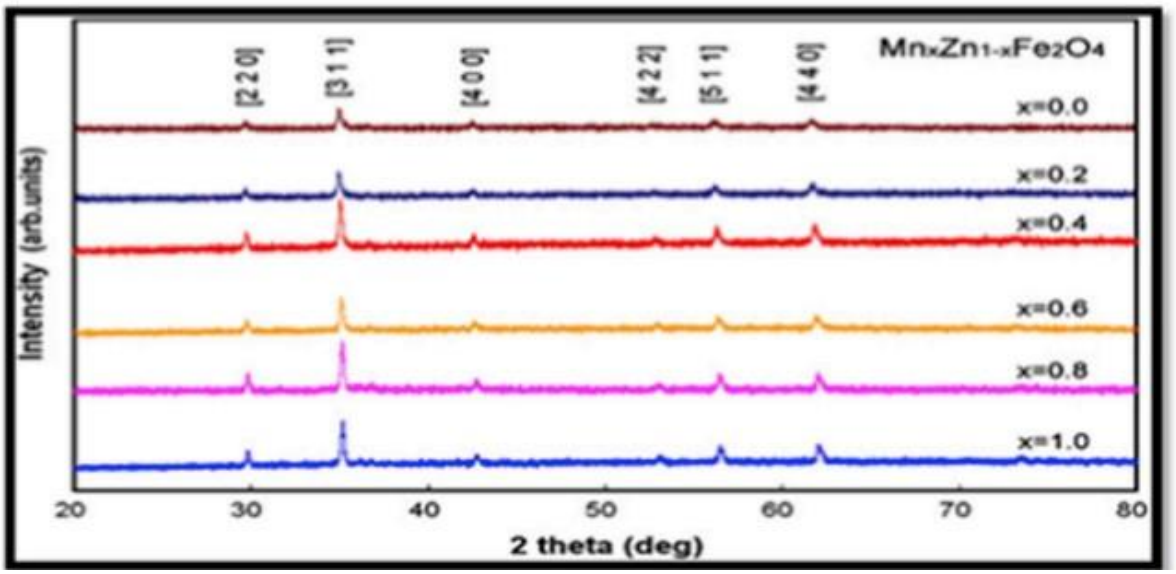
Paper: A review on MnZn ferrites: Synthesis, characterization and applications

Author: Preeti Thakur et al

- The synthesis of MnZn particles has increased in the last ten years and most progress can be seen in the year 2016
- Due to the fascinating properties of MnZn ferrites among the class of soft ferrites like high value of saturation magnetization, low value of coercivity, high initial permeability, narrow size distribution of the ferrite particles, low remenant magnetization, the researchers are taking interest in the synthesis of these ferrites
- The co-precipitation and sol-gel method are the best for getting the fine crystallite size among all synthesis techniques.
- The XRD pattern of the MnZn ferrites has characteristic peaks showing the cubic spinel phase having Fd3m phase group.
- The shape of the prepared ferrite is nearly spherical but some distortion may be observed after doping.
- FTIR spectra confirmed the spinel phase of the ferrite nanoparticles having tetrahedral and octahedral sites.
- The value of saturation magnetization is highest when we synthesize the MnZn ferrites with proper amount of nickel doping by using sol–gel auto combustion method.



Also, for getting the low value of coercivity sol–gel method is preferred. Generally, MnZn ferrites have a lot of applications including biomedical field, electronic devices, for making radar absorbing materials, for making ferrofluids etc.



Paper: Properties of ferrites

Author: Vijaykumar V. Jadhav et al

- Ferrites are combinations of one or more bivalent oxides with trivalent iron oxide.
- Most of them are stoichiometrically balanced, having bivalent and ferric oxides in the ratio of 1:1, while some are deviate in nature.
- A strong magnetic property, relatively low conductivity, low eddy current and dielectric losses, and high permeability are the important properties of ferrite materials.
- Different types of ferrites reveal different chemical formulas and structures due to which there is variation in the properties that enabled them as important candidates for industrial applications

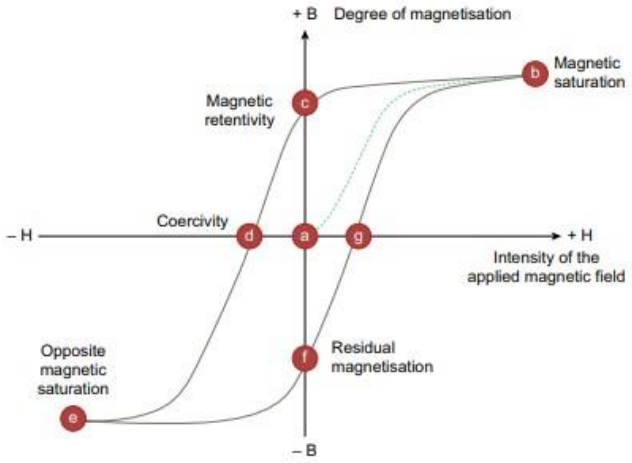


Figure 3.2 General magnetic field (B) versus applied field (H) plot for ferrite material.

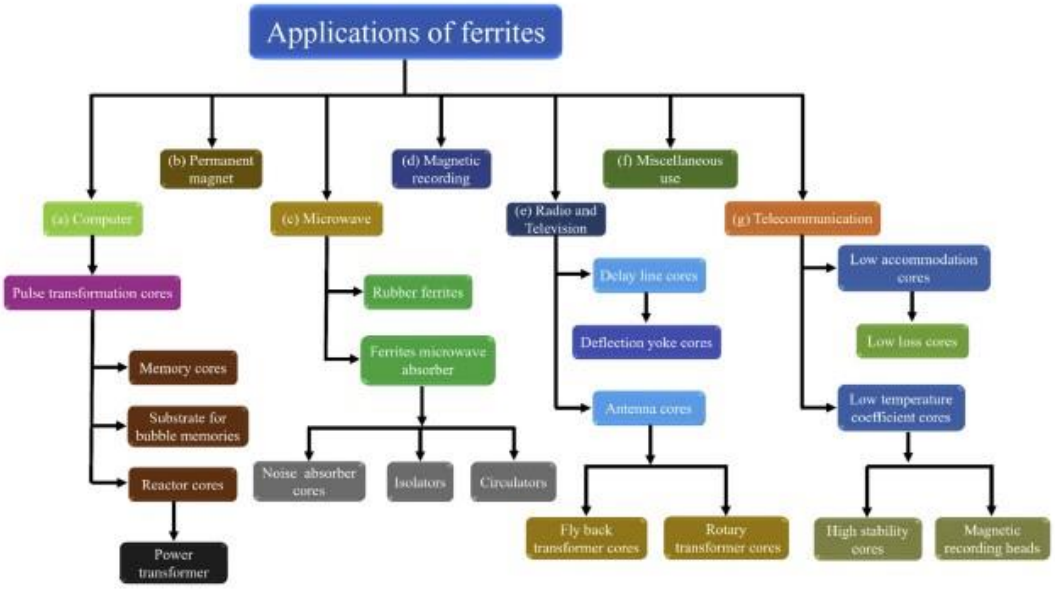


Figure 3.1 Chart displaying applications of ferrites.

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Chapter 3

Methods of preparation

There are two approaches to synthesize nanoparticles: top–down and bottom–up. Both these approaches are shown in Fig. 5(a). In top–down, a bulk material is broken down to get nanosized particles. This method has many limitations like generally metal oxides are used, requirement of very high temperature for the reaction, products are inhomogeneous, presence of impurities, crystal defects, broad size distribution and imperfection in surface structure. In bottom–up approach, small atomic building blocks fit together to produce nanoparticles. This is most favorable method for nanoparticles synthesis as the products in this method are homogeneous, highly pure and have narrow size distribution. Various synthesis techniques are used to prepare MnZn ferrite nanoparticles [152–160]such as sol-gel mthod [161–164], polyol process [165],co-precipitation method [104,166,167], hydrothermal method [113], citrate precursor method [122], solid state reaction method [118], auto-combustion method, ceramic processing method

Sol-gel method

- The sol-gel process is a chemical method for the synthesis of various nanostructures, especially metal oxide nanoparticles.
- In this method, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholysis.
- Since the gel obtained from the hydrolysis process is wet or damp, it should be dried using appropriate methods depending on the desired properties and application of the gel.
- After the drying stage, the produced gels are powdered and then calcined.

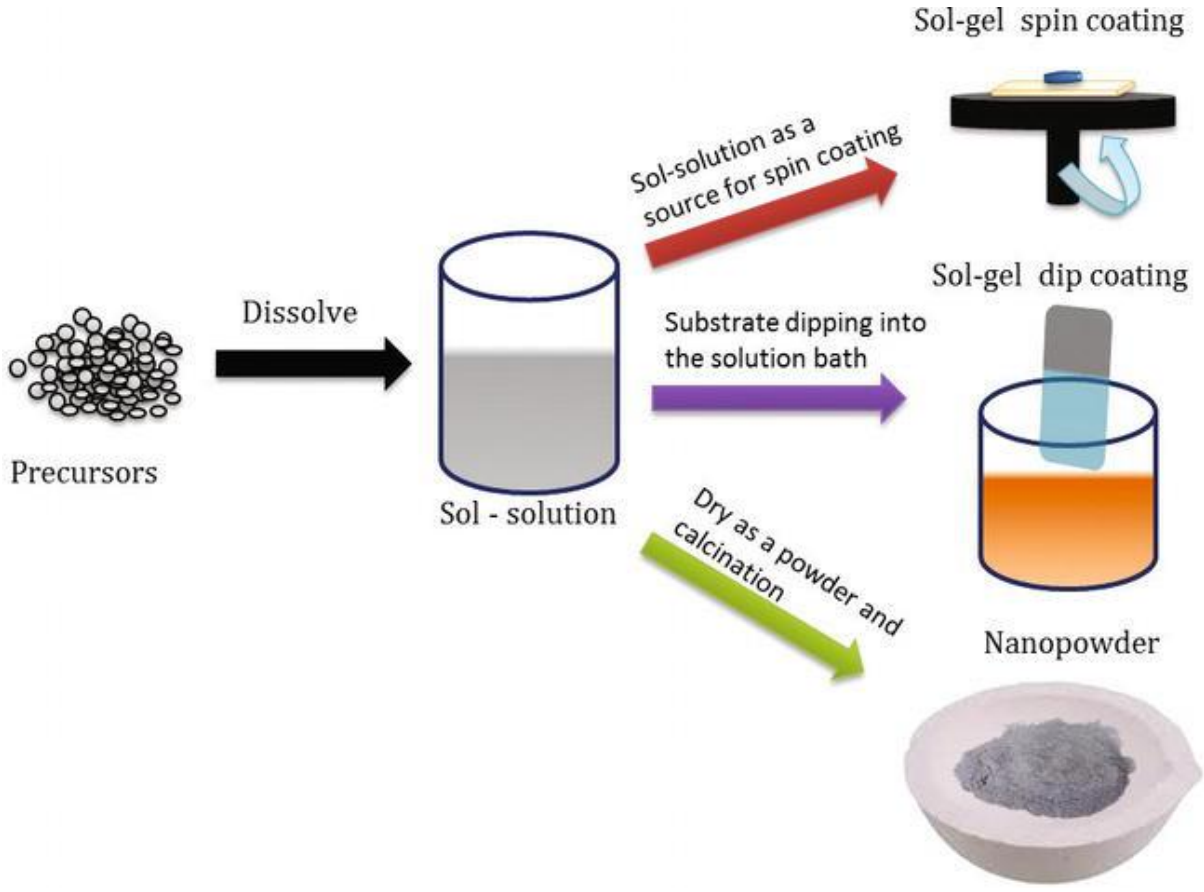


Figure 3:sol-gel method

Hydrothermal method

Hydrothermal synthesis is a method of producing materials by using high-pressure and high-temperature aqueous solutions.Water acts as both the solvent and the reaction medium, facilitating the formation of various compounds.

The hydrothermal environment allows for the synthesis of materials with unique properties and structures that are not easily achievable under standard conditions.The solubility of reactants and products in water varies with temperature and pressure, influencing the formation of different materials.This involves heating of the reactants in a close vessel called Autoclave. autoclave is usually constructed from thick stainless steel to withstood the high press and is fitted with a safety wall .It may be linear with Teflon(Non reactive material).When autoclave is heated the pressure increases and the water remains liquid above its normal boiling temperature of 373 K which is called superheated water .These conditions when pressure is raised above atmospheric pressure and temperature above the boiling temperature are known as “Hydrothermal method” .

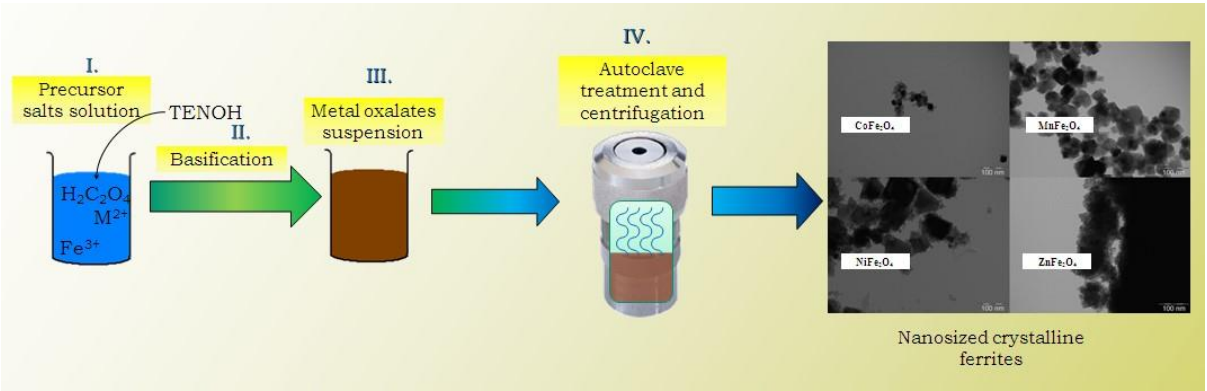


Figure 4:Hydrothermal method

Solvothermal method

- Solvothermal synthesis is a technique similar to hydrothermal synthesis, but it uses organic solvents instead of water as the reaction medium.

- Organic solvents provide a different chemical environment compared to water, leading to the formation of distinct materials and structures.

  Solvothermal reactions occur at elevated temperatures and pressures, facilitating the formation of specific materials.

  The solubility of reactants and products in the organic solvent changes with temperature, influencing the composition and morphology of the synthesized materials.

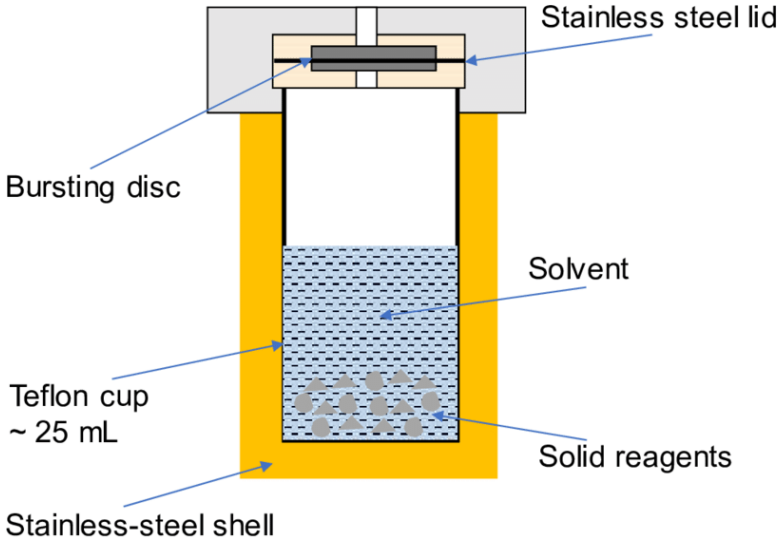


Figure 5:: Solvothermal method

Co-precipitation method

- The synthesis of SFs by coprecipitation method is the most convenient, economic, and less time-consuming, has high mass production, and is frequently employed among all other methods in order to achieve uniform-sized particles.

  In co-precipitation method, reactants are taken in the form of chlorides or nitrates and mixed in distilled water and then suitable precipitating agent such as hydroxides is added as to get precipitates.

- The precipitates are the uniform mixture of reactants in the form of ferrite metals on the atomic scale.

- The precipitates are washed so as to remove the impurities and separated from the mother liquor with the help of centrifuge.

- The obtained precipitates are dried in hot oven to burn the carbonaceous matter leaving a residue of the ferrite metals.

- The residue is grinded to obtain powder. For the growth of suitable nanoparticles pre-sintering and sintering is done at suitable temperature.

- This method is preferred to be the suitable route for synthesizing water dispersible SFs, and a variety of SFs have been synthesized by coprecipitation method including $CoFe_2O_4$, $MnFe_2O_4$, Fe_3O_4, and Sn-doped $MnFe_2O_4$.

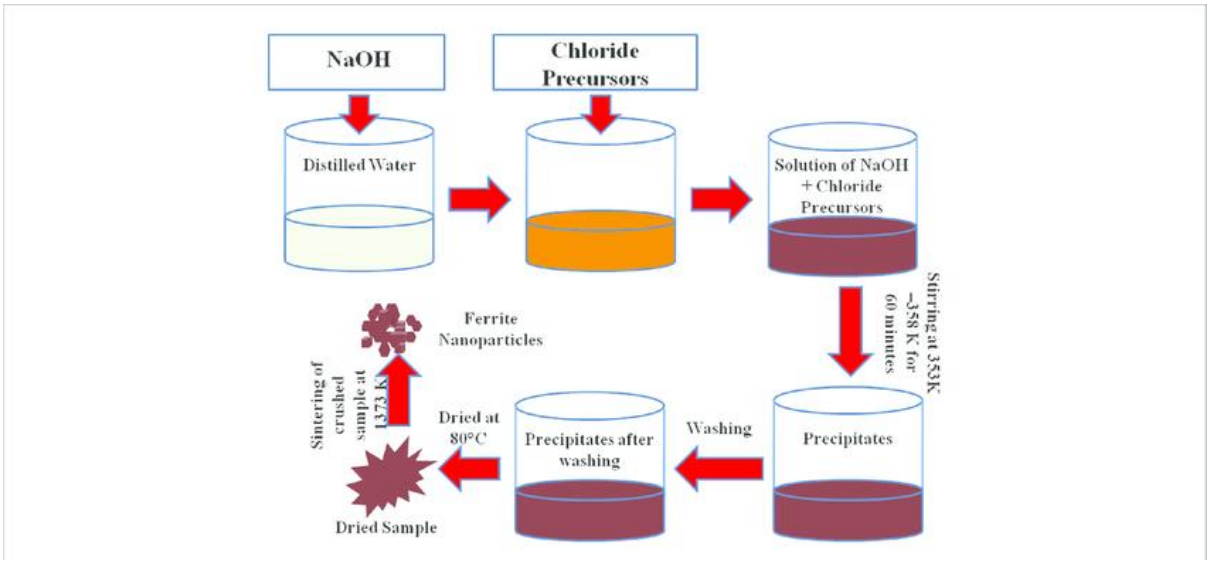


Figure 6:: Co-precipitation method

Why do we prefer MnZn ferrites? MnZn ferrites are preferred over other ferrites due to their low cost and wide range of applications. These ferrites are very important for stress insensitivity and low noise and are generally used for applications where frequency requirements are below 2 MHz. MnZn ferrites are also advantageous due to their almost zero magnetocrystalline anisotropy. In the class of soft ferrites, MnZn ferrites are preferred due to high permeability , saturation induction , low power losses and high magnetic induction [139,140]. MnZn ferrites are of great interest due to their wide range of applications such as hyperthermia applications , power applications , magnetic fluid , high frequency power supply , memory storage devices, TV sets, biomedicines , magnetic resonance, catalysis etc. There is a continuous progress in the size and shape control of MnZn ferrites and also on the morphological and magnetic properties of MnZn ferrites by using different methods of synthesis like sol-gel method [96–98], co-precipitation method , conventional ceramic technique , hydrothermal method, citrate precursor method , solid state reaction method , auto-combustion method , microemulsion method . The effect of doping on the structural and magnetic properties of pure MnZn ferrites is also taken into account.

Auto-Combustion method

Manganese zinc ferrite with composition $Mn_{1-x}Zn_xFe_2O_4$ with x =(0, 0.2, 0.4, 0.6 ,0.8 ,1) were prepared using the combustion method. The metals salts of Mn, Zn, and Fe along with nitrilotriacetic acid and urea were dissolved in 400 ml of double distilled water with constant stirring with constant heating to obtain a clear solution. The solution was further heated with constant stirring until the volume was reduced to 100 ml. This solution was transferred into a steel plate with a flat bottom surface for uniform heating. As the heating processes continued, the solution turned into a dry mass that caught fire as the ignition temperature was reached. The dry ash obtained at the end of the combustion process was crushed into a fine powder and was used for characterization purposes.

Figure 7:Auto-combustion method

Method of preparation of thin films

Spin coating

- Spin coating is a method to prepare uniform and homogeneous thin films onto the flat substrates.Spin coater works on the principal of centrifugal force.

  The machine used here is commonly called spin coater or spinner.

- The working of this technique is divided in 4 steps deposition:- spin up, spin down and evaporation

  Deposition – The solution is put on the centre of substrate with the help of pipette. It has to be put in such way that no bubbles are formed.

  Spin-up – during this process the substrate is spun at high rpm and because of centrifugal force the solution will uniformly spread out on the substrate. Usually 1000-6000 rpm. Here most of the solution is expelled out and it becomes thin layer because of viscous force.

  Spin-down – The transition to this process is not abrupt, the speed is reduced slowly and colour of the fluid starts changing indicating that evaporation of solvent has started.

- **Evaporation** – Here evaporation increases because of increase in viscous forces. The fluid outflow is stopped. The rate of evaporation is determined by solvent volatility.

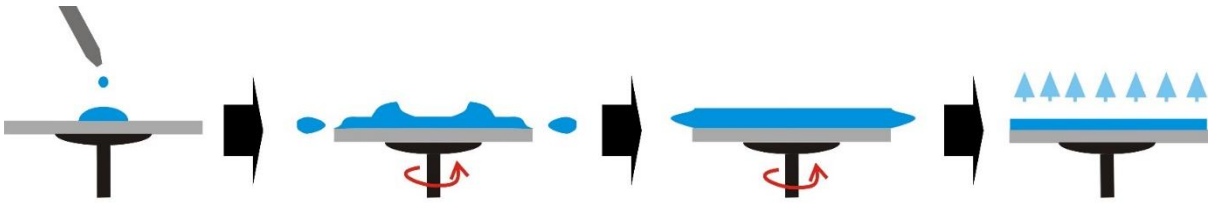


Figure 8:Spin coating method

Spray pyrolysis

- A simple and inexpensive method of synthesizing thin and thick film, metal and metal oxide coating in large scale.
- An aerosol process that atomizes a solution and heats the droplets to produce solid particles.
- Pyro=heat and lysis=breaking, pyrolysis-change under the action of heat.
- Here complex molecules are broken into simpler units by heating.
- Basically the solution will by sprayed as an aerosol accompanied by heating eventually leading to the formation of solid particles.
- Initially, the precursor(material generally salts of metals whose reduced particles we want) are mixed with the liquid (typically) water to form the solution.

  This solution is then fed to the atomizer which will make aerosol droplets which will be driven to the thermolysis(heating) chamber with some initial velocity given by the atomizer. Here carrier gases (N, H, Ar etc) are also fed to the droplets which helps carry the droplets into the heater.

  In the heater, reaction gases may be introduced if the desired particles needs to be infused if desired.

  After the infusion, the droplets move to the furnace where thermolysis occurs-breakdown of droplets in presence of heat. Here, only the solute remains and solvent evaporates.

  After thermolysis, the solutes then move to the sintering furnace. This furnace has a

higher temperature then the thermolysis furnace. The particles are heated and all the solvent is removed and the particles also become dense and large.

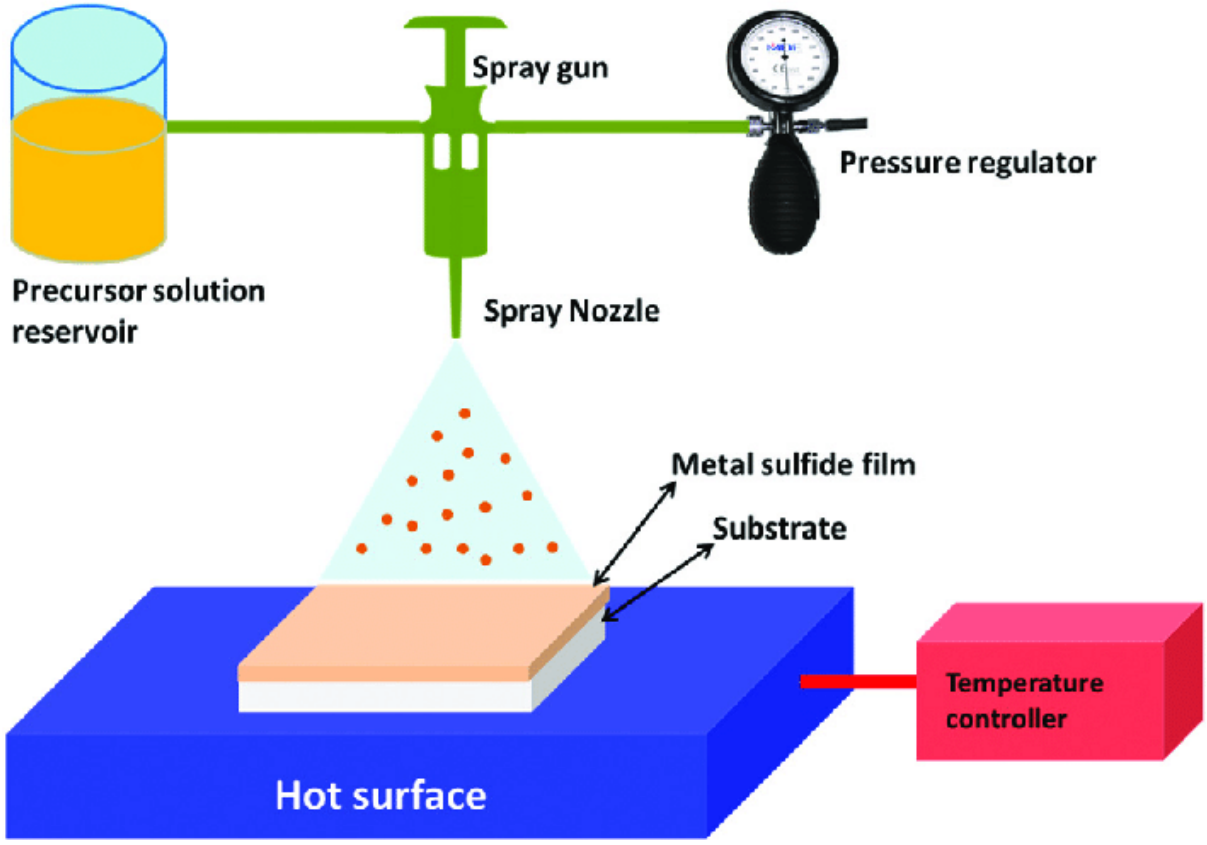


Figure 9: Spray pyrolysis

RF sputtering,

RF sputtering or radio frequency sputtering, is a variant of physical vapor deposition (PVD) used for depositing thin films onto substrates. In RF sputtering, a radio frequency power source is used to generate plasma from a gas (usually argon) in a vacuum chamber. The plasma contains positively charged ions and free electrons. When a negative voltage is applied to a target material (the material to be deposited), typically a metal or metal oxide, in the presence of the plasma, the ions are accelerated towards the target surface. Upon collision with the target surface, the ions transfer momentum to the target atoms, causing them to be ejected or sputtered from the target material. These sputtered atoms then travel across the vacuum chamber and deposit onto the substrate, forming a thin film.

Here are some key aspects of RF sputtering:

1. **Plasma Generation**: RF sputtering utilizes radio frequency power (typically in the MHz range) to generate a plasma from a gas (usually argon) within the vacuum chamber. The plasma consists of ions and free electrons, which facilitate the sputtering process.

2. **Target Material**: The target material, often made of metals such as aluminium, titanium, or chromium, or metal oxides like indium tin oxide (ITO), is the source of the atoms that will form the thin film. The choice of target material determines the composition and properties of the deposited film.

3. **Sputtering Process**: The negatively biased target attracts positively charged ions from the plasma. Upon collision with the target surface, the ions transfer their kinetic energy to the target atoms, causing them to be ejected or sputtered. These sputtered

atoms then travel across the vacuum chamber and deposit onto the substrate, forming a thin film.

4. **Film Thickness Control**: The film thickness can be controlled by adjusting parameters such as sputtering time, target-to-substrate distance, and RF power. Monitoring techniques such as quartz crystal microbalances or optical interferometry can be used for real-time thickness control and measurement.

5. **Advantages**:

    - Good adhesion and uniformity of deposited films.
    - Wide range of materials can be sputtered, including metals, semiconductors, and insulators.
    - High deposition rates compared to some other PVD techniques.
    - Suitable for large-area deposition and batch processing.

6. **Limitations**:

    - Line-of-sight deposition can result in non-uniform film thickness on complex geometries.
    - Target material utilization efficiency may be lower compared to other sputtering techniques.
    - Higher equipment and maintenance costs compared to some other thin film deposition methods.
    - Susceptible to target poisoning or contamination, affecting film quality and deposition rate.

Chapter 4

Characterisation techniques

X-ray diffraction

- X-Ray diffraction analysis provides detailed information about the crystallographic structure, chemical composition, and physical properties of a material.
- It is based on the constructive interference of monochromatic X-rays and a crystalline sample.

XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material

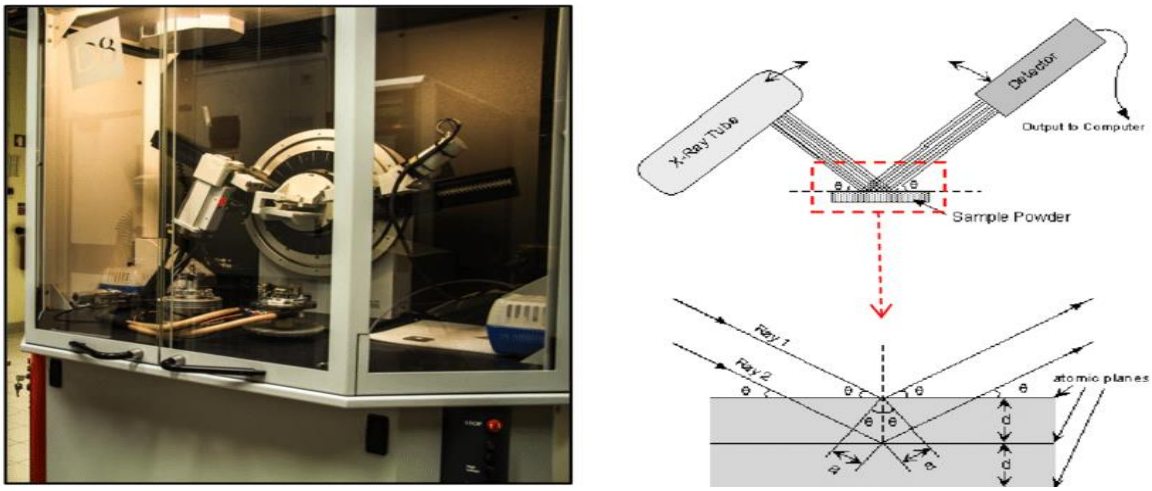


Figure 10:X-ray diffraction

Application

- measurement of sample purity
- determination of unit cell dimensions

- characterization of crystalline materials and determine structural properties
- Lattice parameters- Strain- Grain size- Epitaxy- Phase composition- Preferred orientation
- characterize thin films samples and measure the thickness of thin films and multi-layers
- Determine atomic arrangement
- identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically

Scanning electron microscopy

- **Scanning electron microscope** (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons.

- The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample.

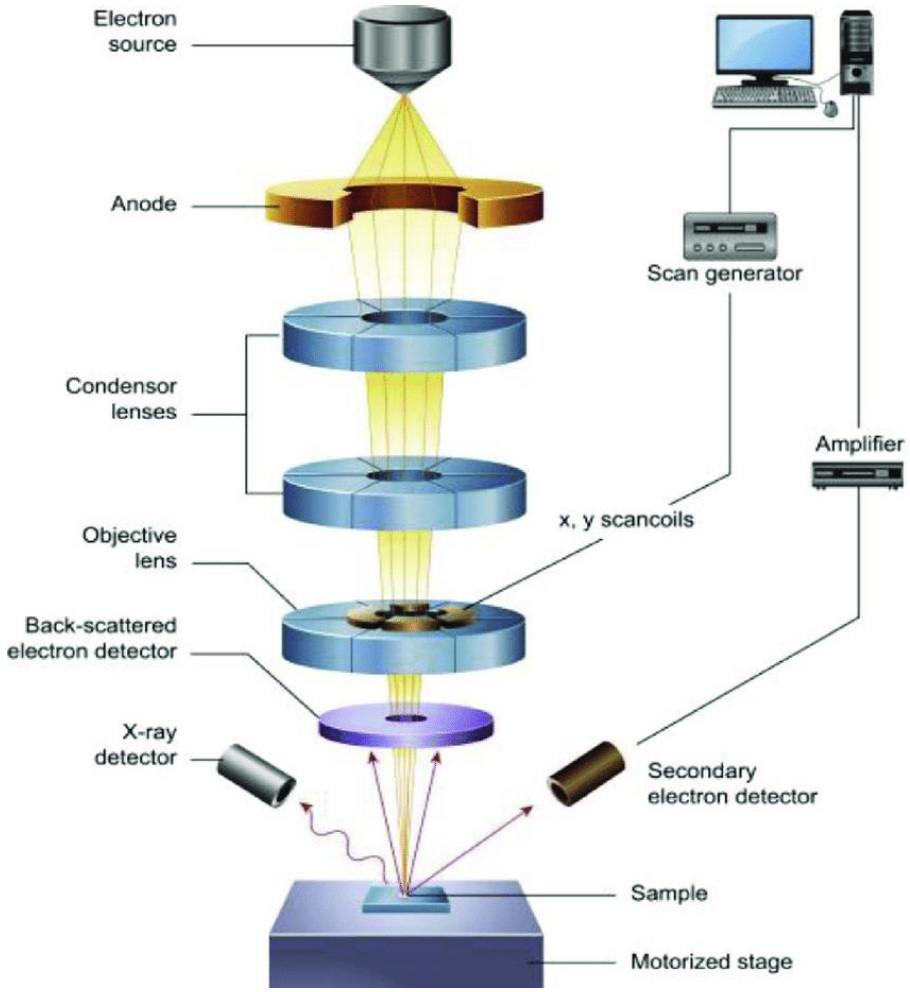


Figure 11 : Scanning electron microscope

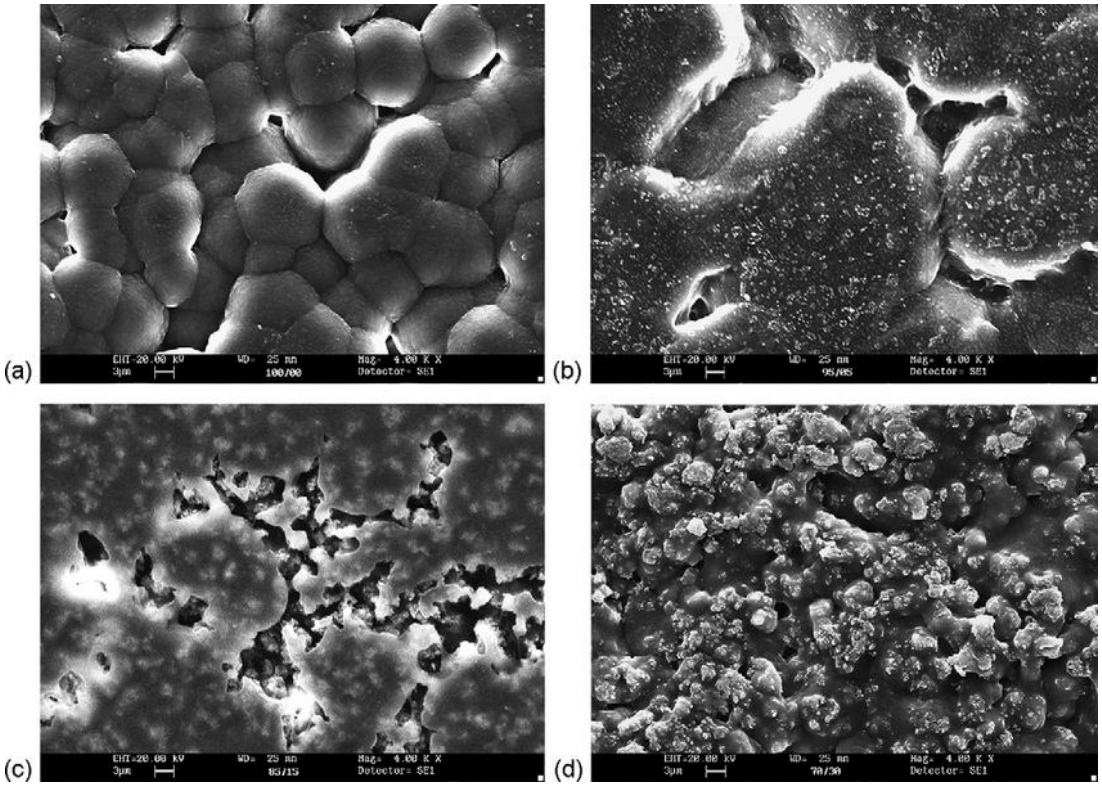


Figure 12:SEM images

Transmission electron microscopy

- **Transmission electron microscopes** (TEM) are microscopes that use a particle beam of electrons to visualize specimens and generate a highly-magnified image.
- TEMs employ a high voltage electron beam in order to create an image. An electron gun at the top of a TEM emits electrons that travel through the microscope's vacuum tube.
- TEM employs an electromagnetic lens which focuses the electrons into a very fine beam.
- This beam then passes through the specimen, which is very thin, and the electrons either scatter or hit a fluorescent screen at the bottom of the microscope.
- An image of the specimen with its assorted parts shown in different shades according to its density appears on the screen.
- This image can be then studied directly within the TEM or photographed.

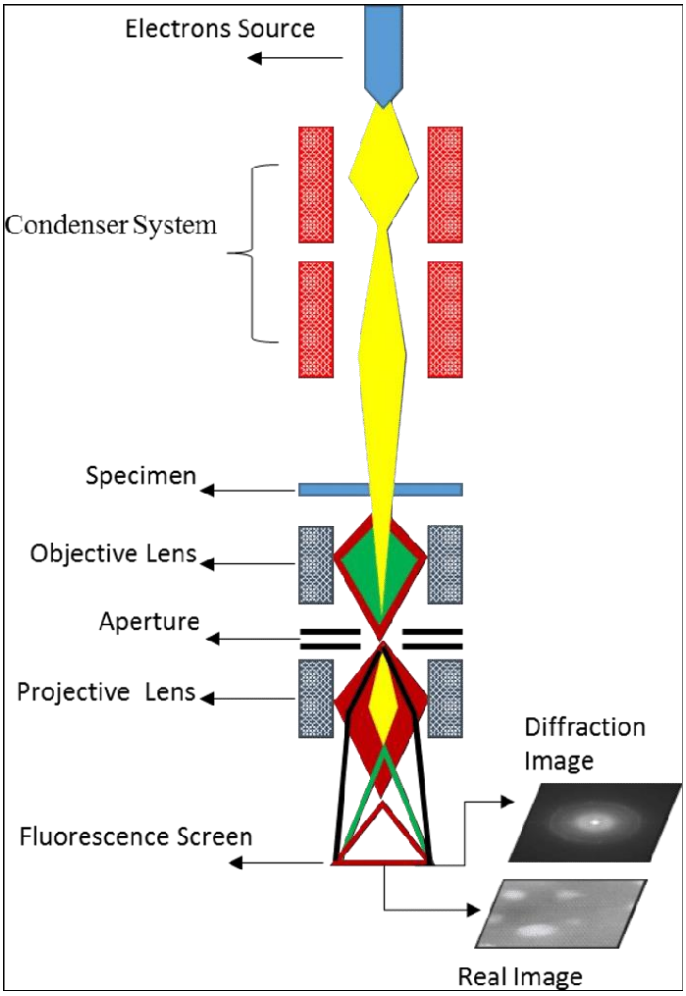


Figure 13: Transmission electron microscopy

UV-Visible Spectroscopy

Since this spectroscopy technique relies on the use of light, let's first consider the properties of light. We know that light has a certain amount of energy which is inversely proportional to its wavelength. Thus, we know that shorter wavelengths of light carry more energy and longer wavelengths carry less energy. A specific amount of energy is needed to excite electrons in a substance to a higher energy state which we can detect as absorption. Different specific amount of energy is required to promote the electrons to a higher energy state from electrons in different bonding environments. This is why the absorption of light occurs for different wavelengths in different substances. We are able to see a spectrum of visible light, from approximately 380 nm, which is violet, to 780 nm, which is red. UV light has wavelengths shorter than that of visible light to approximately 100 nm. Therefore, light can be described by its wavelength, which can be useful in UV-Vis spectroscopy to analyse or identify different substances by locating the specific wavelengths corresponding to maximum absorbance. The absorption by a molecule of UV or visible light radiation result s in transition between molecule's energy level

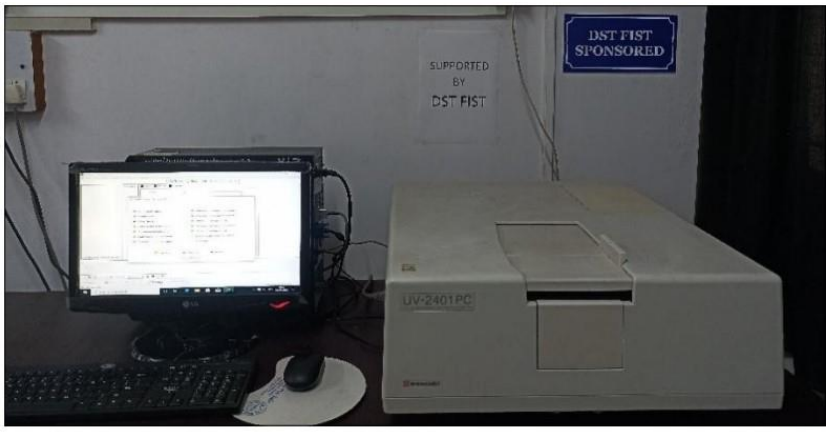


Figure 14:UV-v is spectroscopy

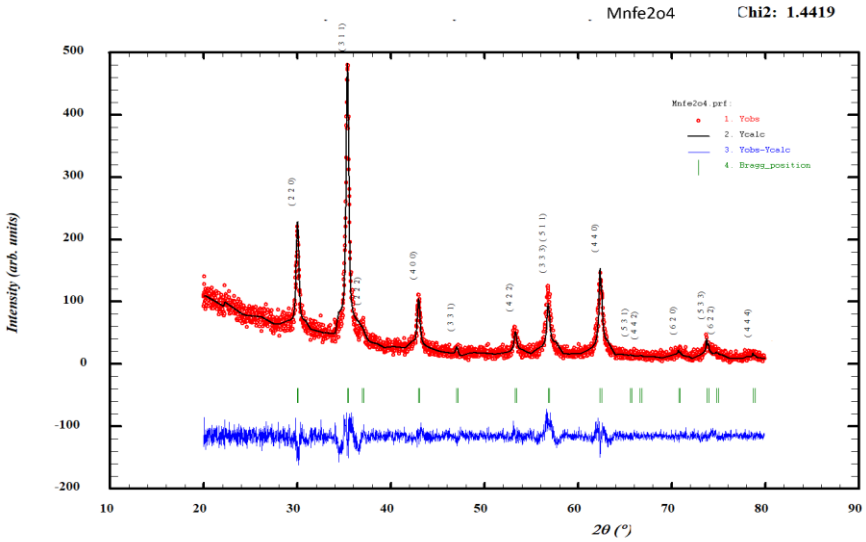
Raman Spectroscopy

Raman spectroscopy belongs into the category of vibrational spectroscopy which is a powerful tool to characterize the structure of various kinds of materials. It chemically analyses the sample by using light to excite molecular vibration, and interpreting this interaction afterwards. It is based on the inelastic scattering of light that occurs when matter is irradiated by light. As the change of wavelength is very small compared to the wavelength of the irradiating light, the change of wavelength is most easily observed when using monochromatic light sources. After this monochromatic light gets interacted with the sample, a very small part of it has changed its wavelength. This is called as the Raman effect which was discovered by C.V. Raman in 1930 which opened the door to a new kind of spectroscopy which is Raman spectroscopy. Raman spectroscopy did not really take off however, until the discovery of the laser thus, the use of monochromatic light plays an important role. The sample is irradiated with a laser and some of the scattered light is analysed with a spectrograph. At the end Raman spectrum is obtained which shows the characteristic signals or “bands” for the material under investigation.

Chapter 5

Result and discussion

X-ray analysis



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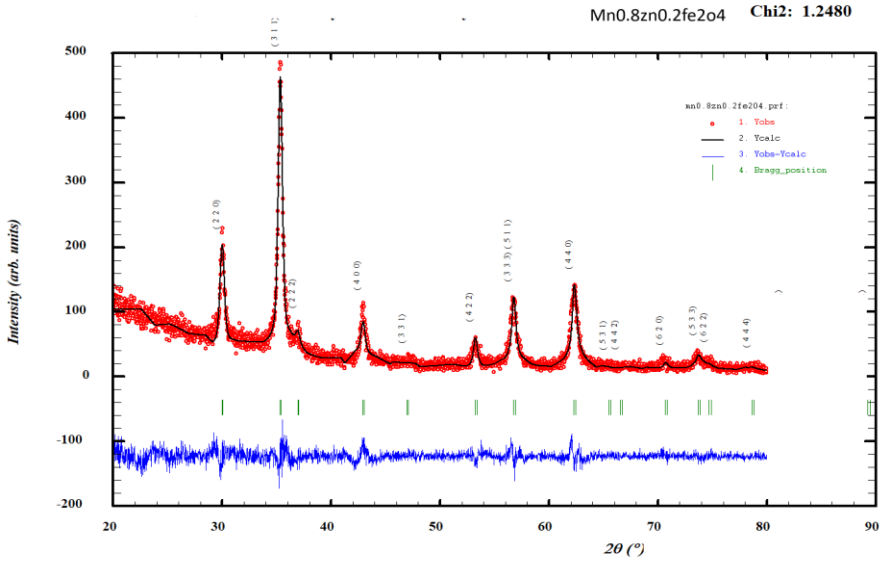

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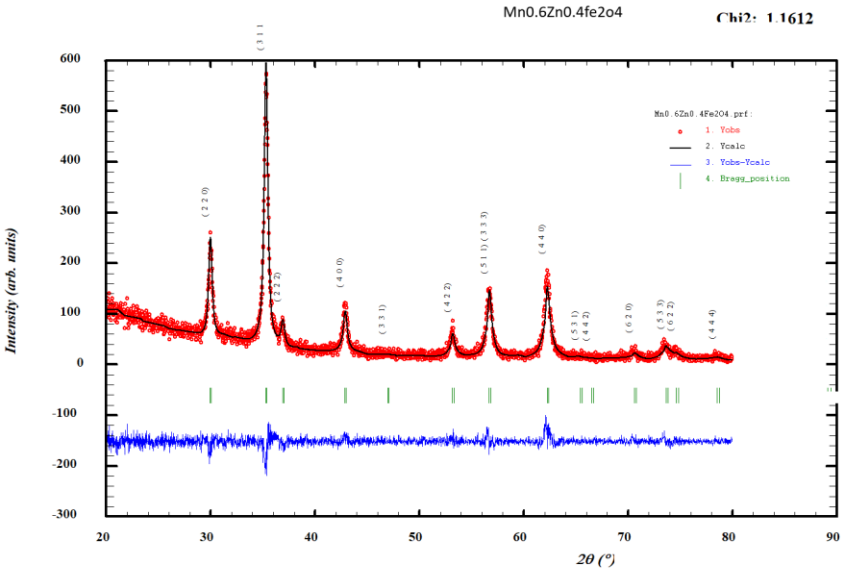
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3. Yobs-Ycalc
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Intensity (arb. units)
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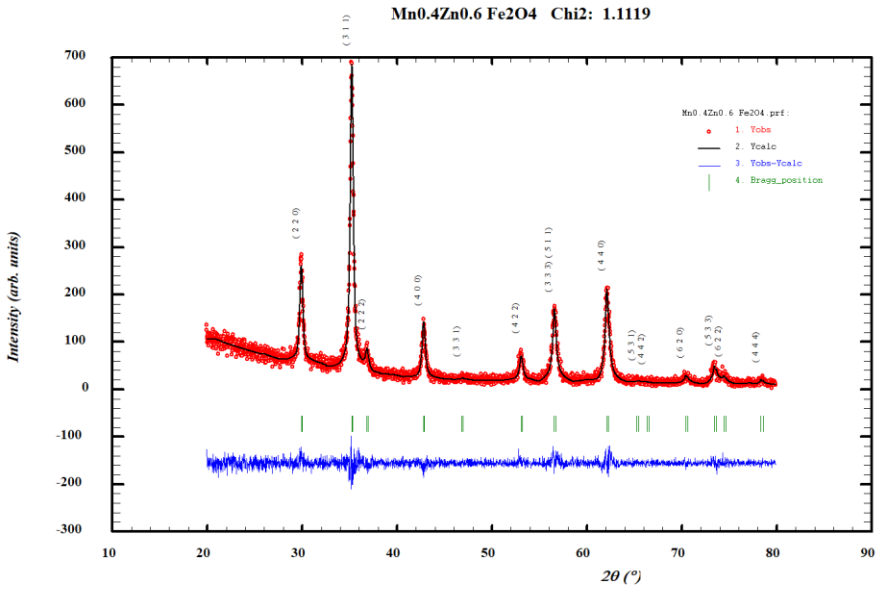
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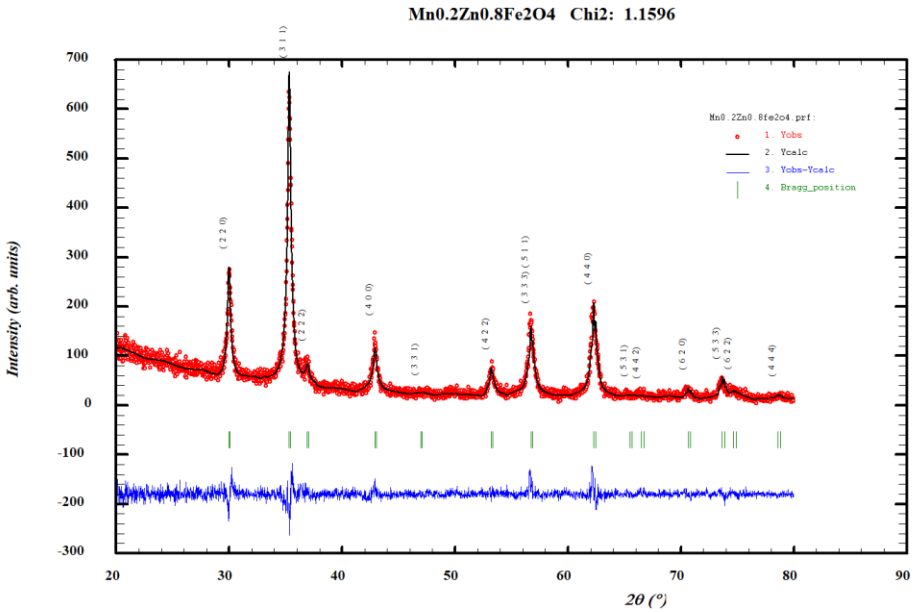

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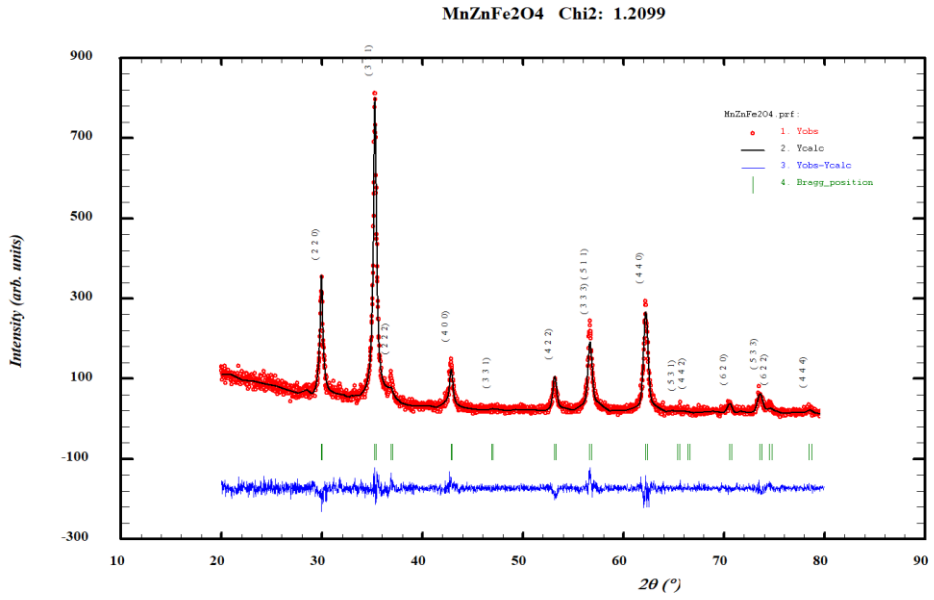


(f)

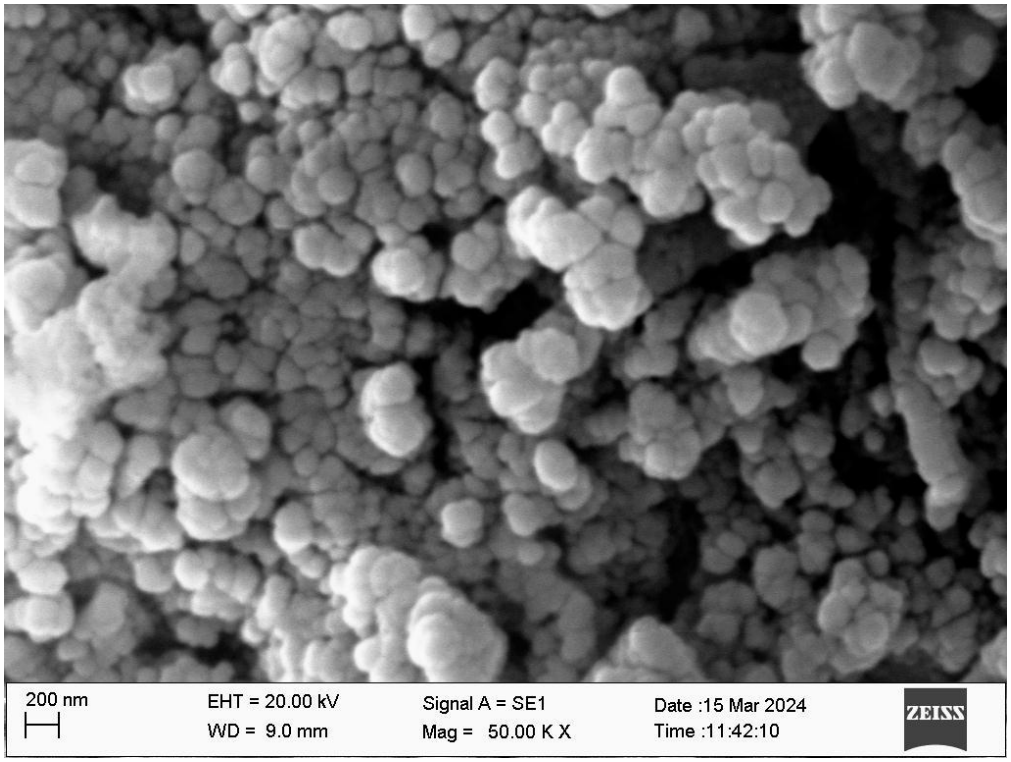
Figure 15:XRD pattren

(a) MnFe2O4 b) Mn0.8Zn0.2Fe2O4 c) Mn0.6Zn0.4Fe2O4 d) Mn0.4Zn0.6Fe2O4 e) Mn0.2Zn0.8Fe2O4 f) ZnFe2O4

	lattice parameter	crystalline size	crystalline strain	RF fcator	FWHM
composition		(nm)			
MnFe2O4	8.4173	16	0.368959511	14.2	0.471
Mn0.8Zn0.2Fe2O4	8.4241	14	0.423900388	12.5	0.54005
Mn0.6Zn0.4Fe2O4	8.4307	15	0.406717842	12.9	0.51768
Mn0.4Zn0.6Fe2O4	8.4491	17	0.355196441	11.9	0.45211
Mn0.2Zn0.8Fe2O4	8.4269	15	0.407595676	11.4	0.51908
ZnFe2O4	8.4378	16	0.366210066	11.2	0.46595

cation distribution				
Mn1-xZnxFe2O4		octahedral	tetrahedral	
	x=0			
	x=0.2			
	x-0.4			
	x-0.6			
	x=0.8			
	x-1			

Scanning electron microscopy



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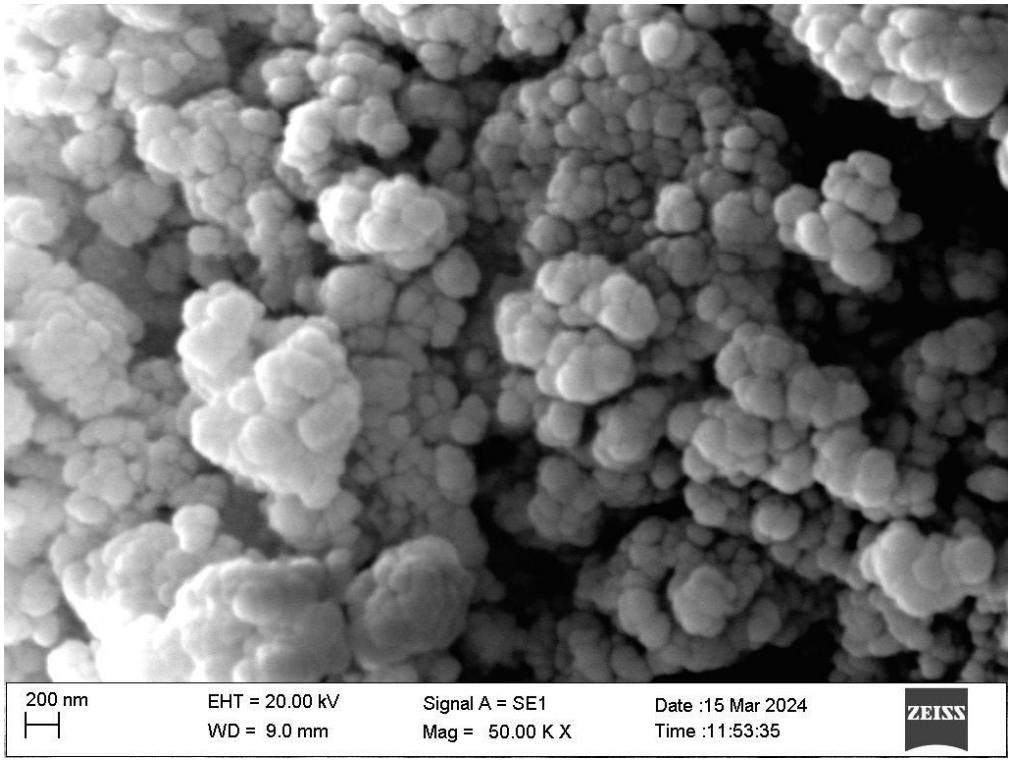

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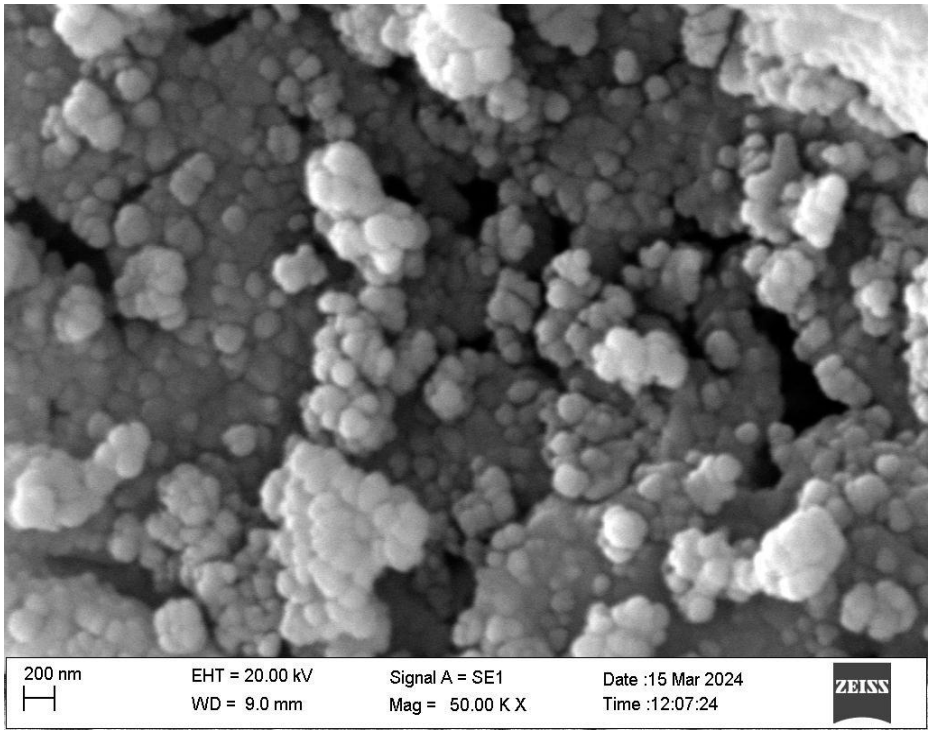
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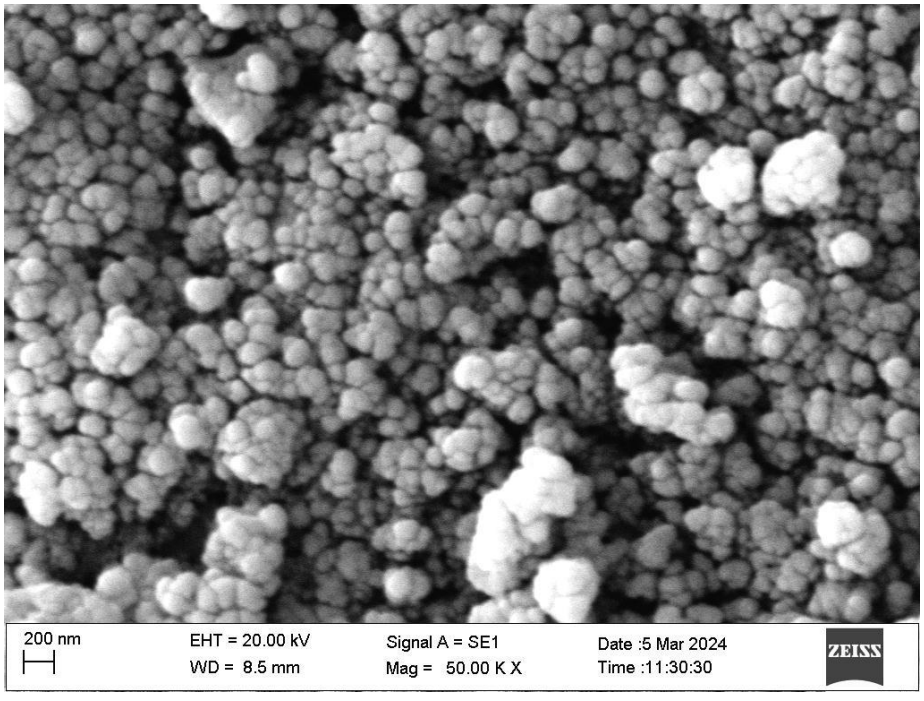
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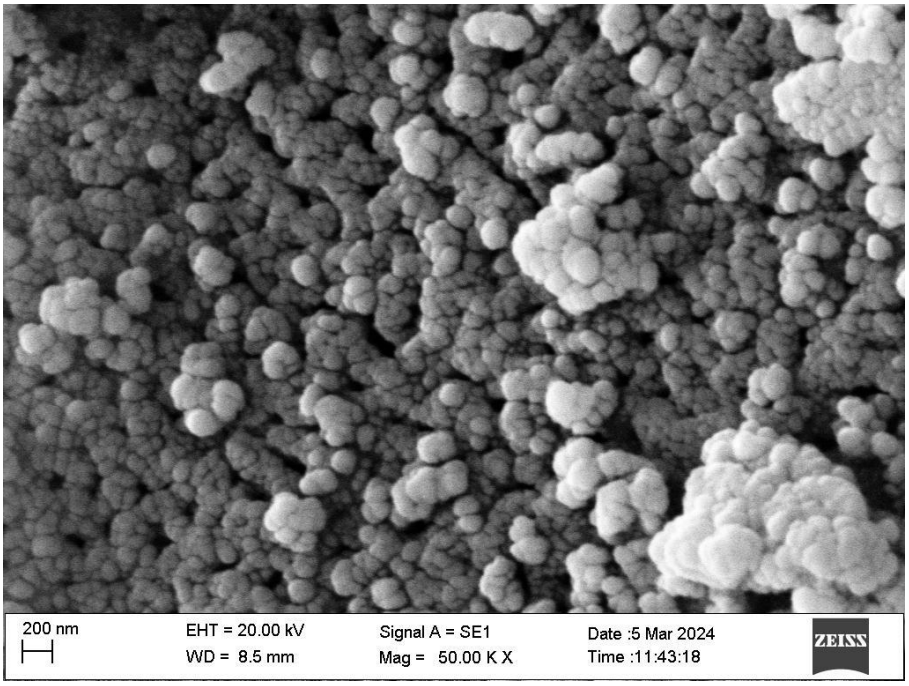
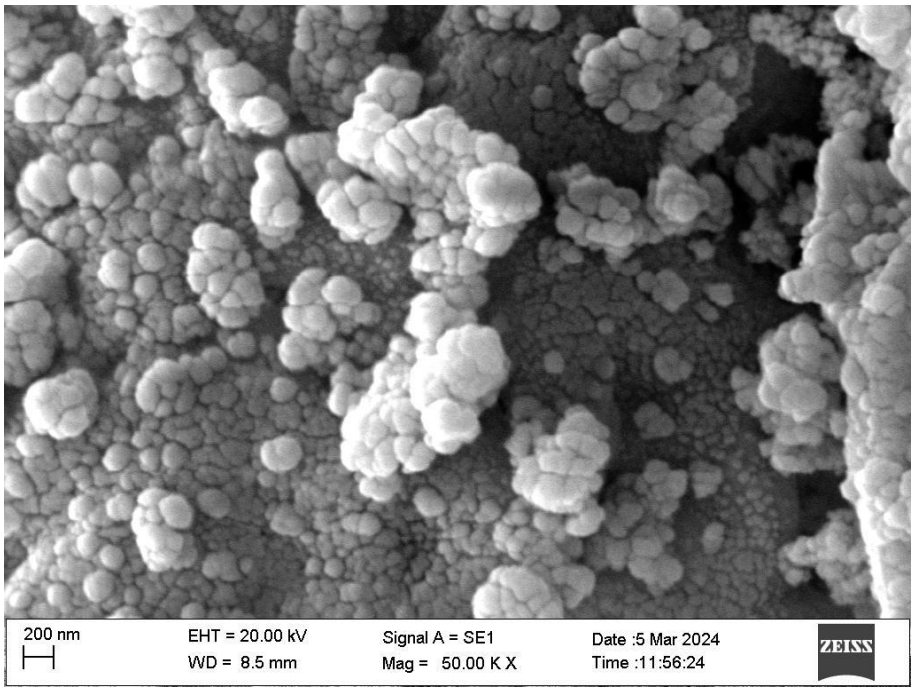
(d)



(e)

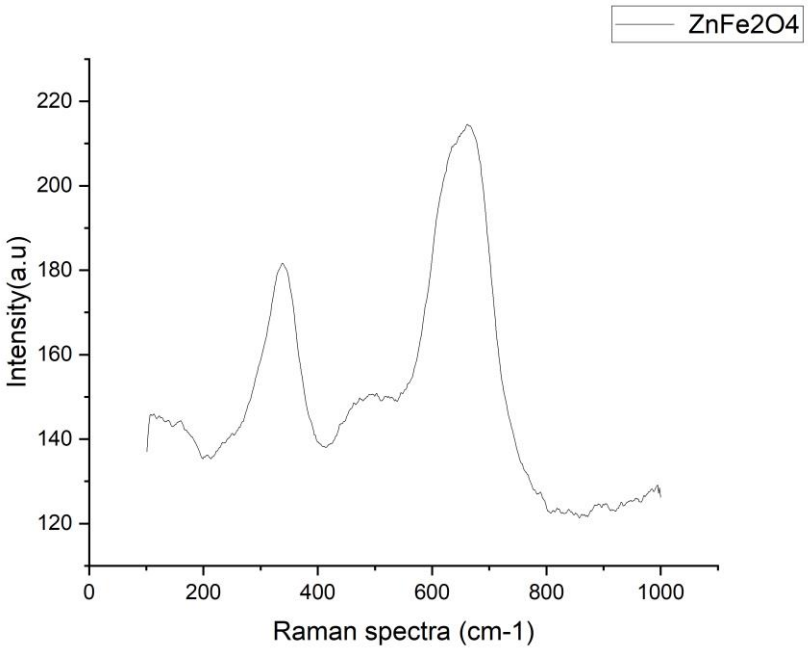


(f)

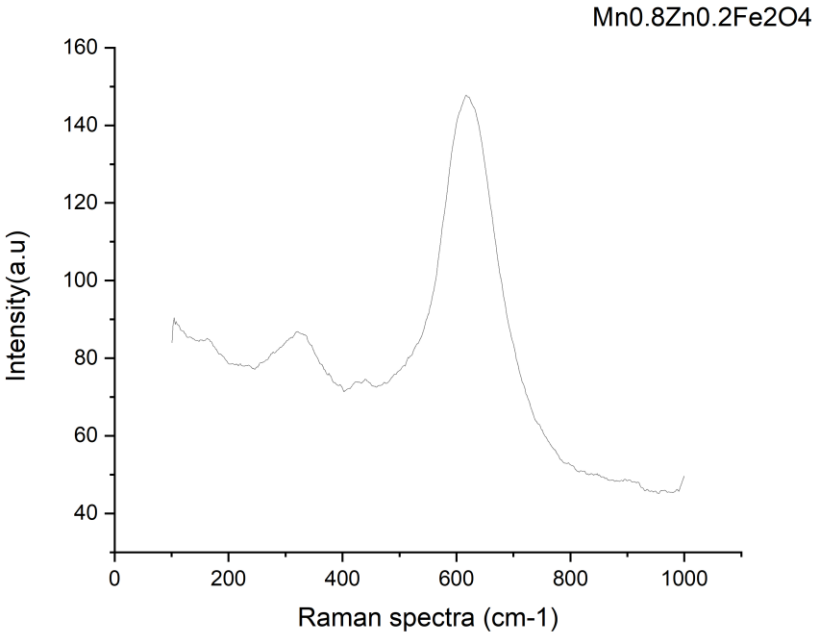
Figure 16:SEM images

a) $MnFe_2O_4$ b) $Mn_{0.8}Zn_{0.2}Fe_2O_4$ c)$Mn_{0.6}Zn_{0.4}Fe_2O_4$ d)$Mn_{0.4}Zn_{0.6}Fe_2O_4$ e)$Mn_{0.2}Zn_{0.8}Fe_2O_4$ f)$ZnFe_2O_4$

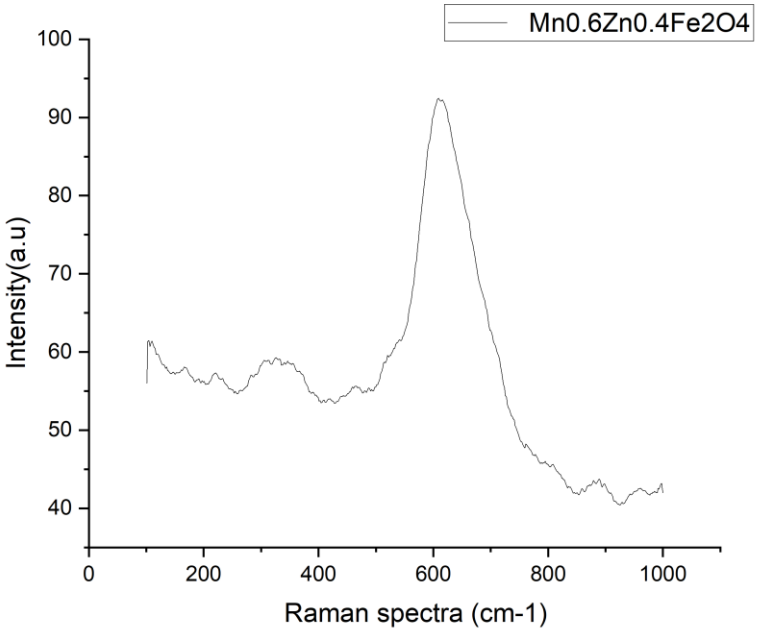
Raman spectroscopy



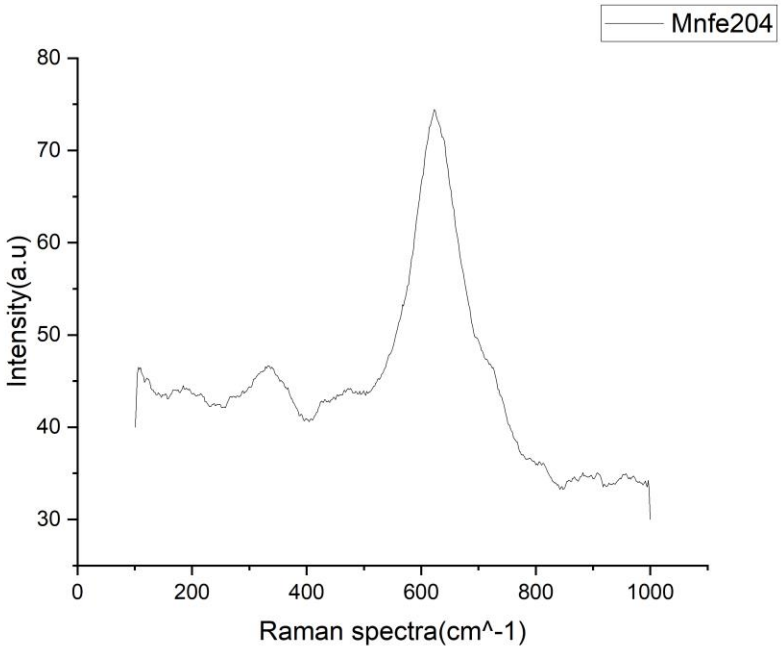
(a)



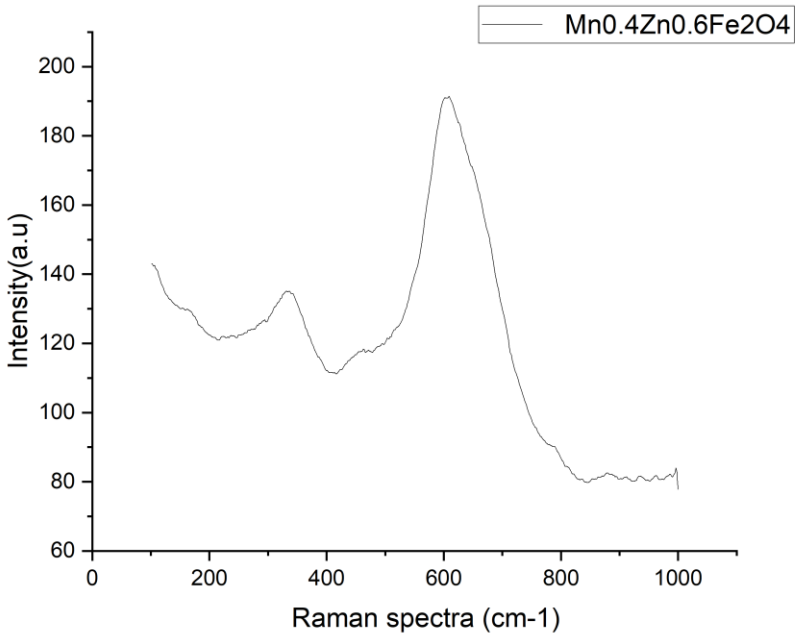
(b)


Mn0.6Zn0.4Fe2O4
Intensity(a.u)
Raman spectra (cm-1)
100
90
80
70
60
50
40
0
200
400
600
800
1000

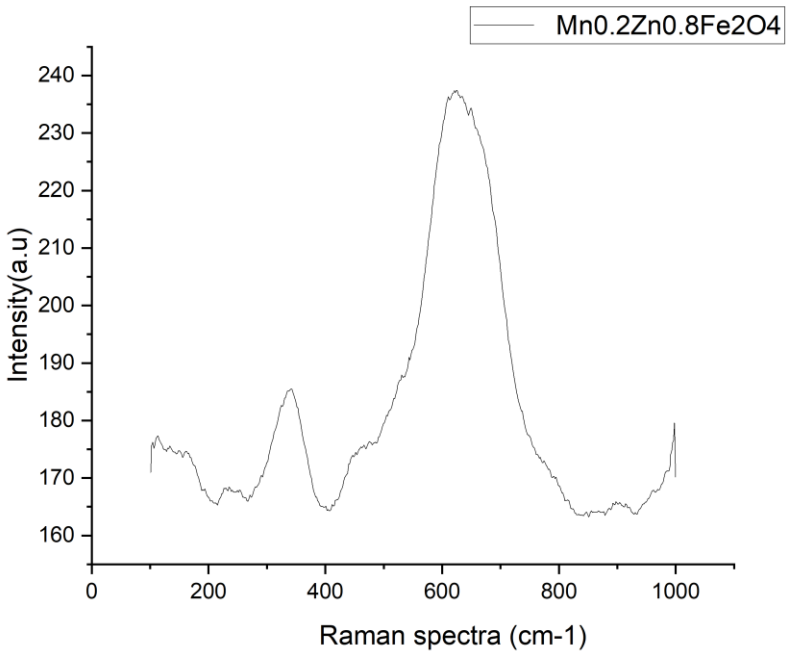
(c)


Mnfe204
Intensity(a.u)
Raman spectra(cm^-1)
80
70
60
50
40
30
0
200
400
600
800
1000

(d)


Mn0.4Zn0.6Fe2O4
Intensity(a.u)
Raman spectra (cm-1)
200
180
160
140
120
100
80
60
0
200
400
600
800
1000

(e)


Mn0.2Zn0.8Fe2O4
Intensity(a.u)
Raman spectra (cm-1)
240
230
220
210
200
190
180
170
160
0
200
400
600
800
1000

(f)

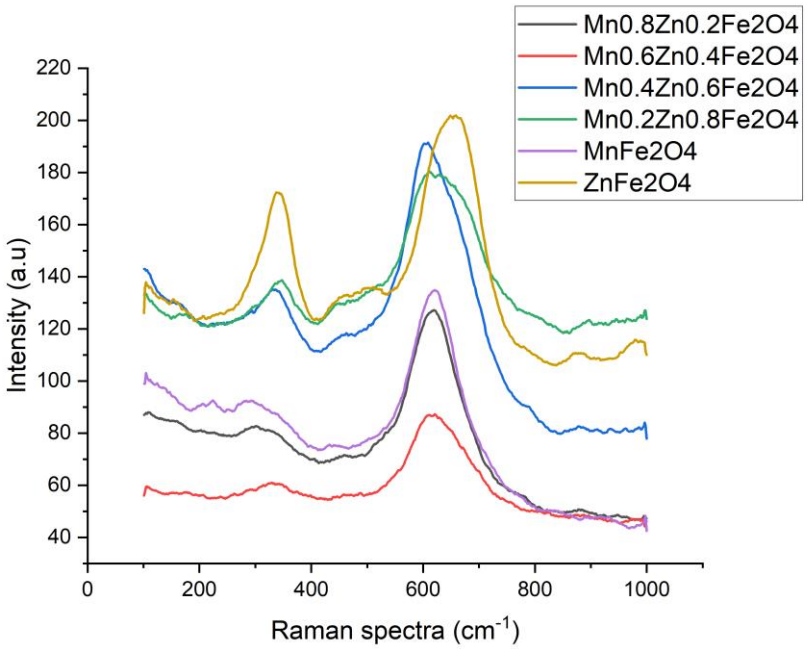


Figure 17:Raman spectra for $Mn_{1-x}Zn_xFe_2O_4$

a) MnFe2O4 b) Mn0.8Zn0.2Fe2O4 c)Mn0.6Zn0.4Fe2O4 d)Mn0.4Zn0.6Fe2O4 e)Mn0.2Zn0.8Fe2O4 f)ZnFe2O4

Dielectric constant

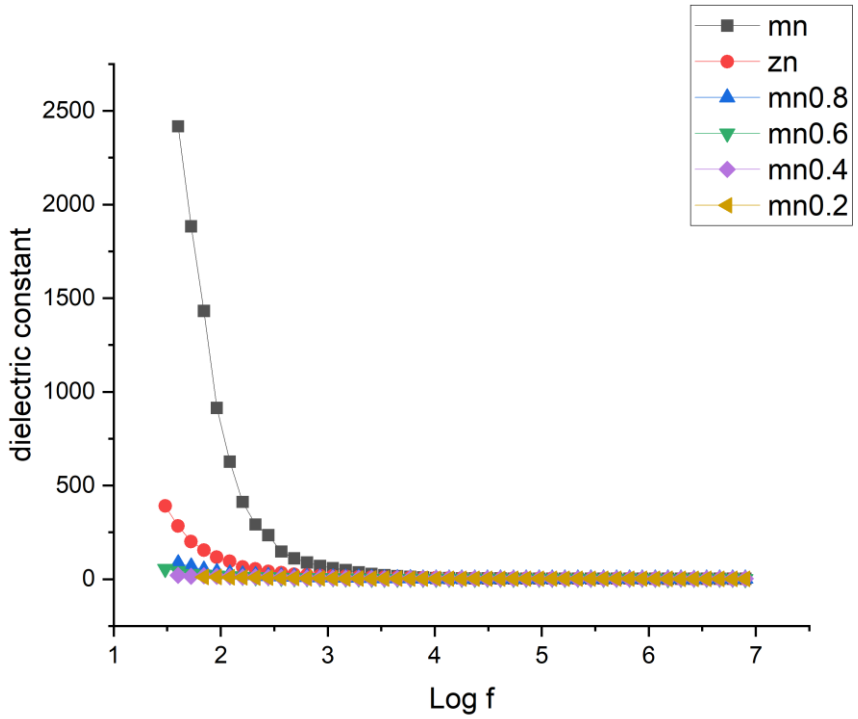


Figure 18:Dielectric constant of $Mn_{1-x}Zn_xFe_2O_4$

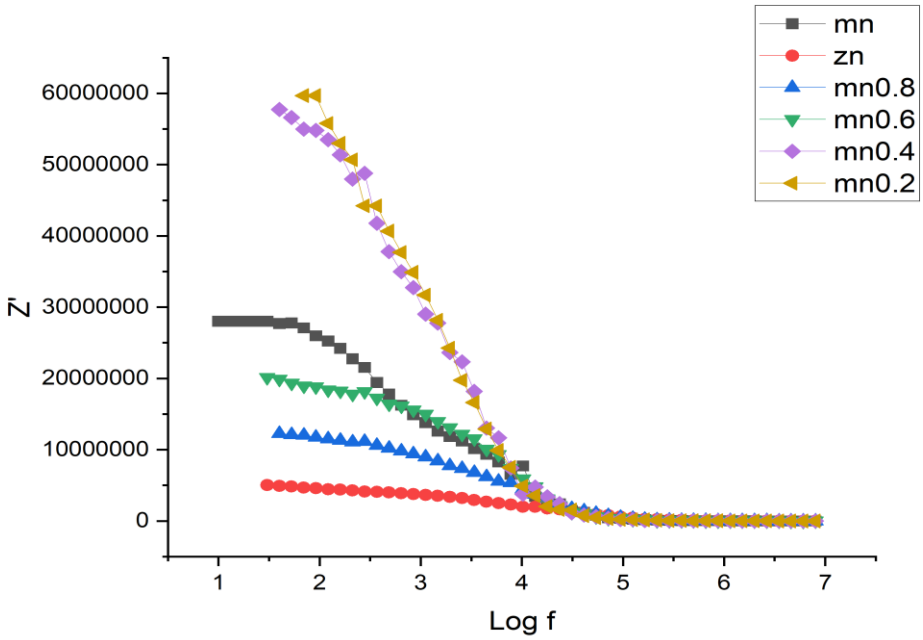


Figure 19: Real part of impedance

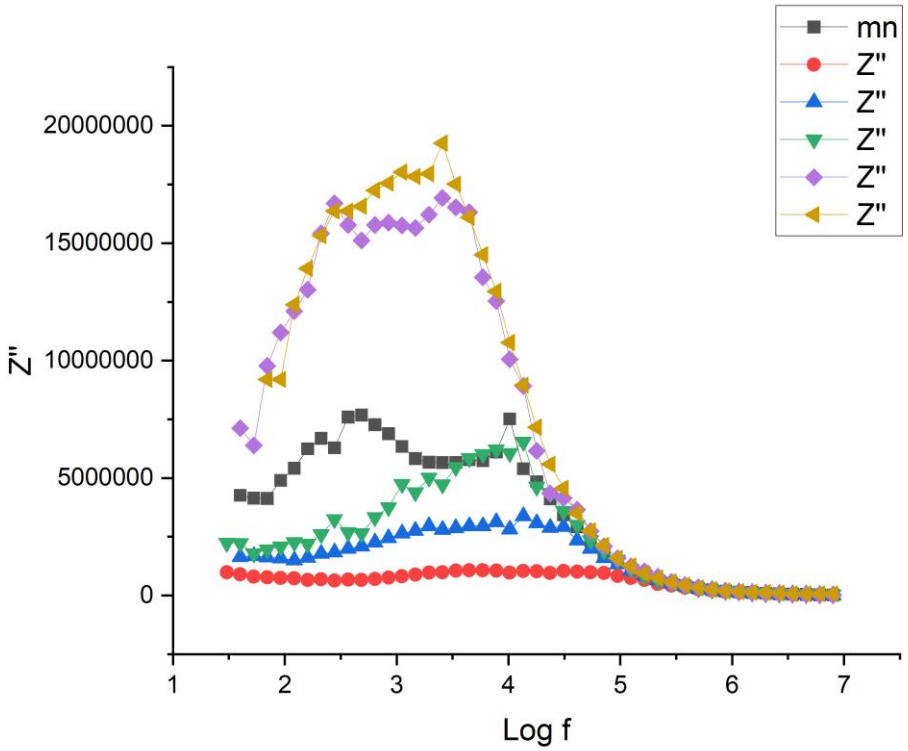


Figure 20:imagenary part of impedance

Conclusion

Mn Zn ferrite nanoparticles with chemical composition $Mn_{1-x}Zn_xFe_2O_4$ (x=0, 0.2, 0.4, 0.6, 0.8, 1) was successfully synthesised using combustion method. The XRD pattern indicated the presence of a cubic spinel phase having Fd-3m space group with the crystallite size ranging between 14 and 17 nm. Raman spectra confirmed the spinel phase of the ferrite nanoparticles having tetrahedral and octahedral sites. The SEM images showed that all the samples contained nearly spherical particles, large agglomerates were seen. The dielectric data shows that at the lower frequency the samples shows the higher dielectric constant and it decreases as the frequency increases.. Mn Zn ferrites have a lot of applications including biomedical field, electronic devices and gas sensers etc. The electrical properties of Mn ferrites can be enhanced by doping other metals such as zinc to make them suitable for use in different application. For enhancing the applications of MnZn ferrite nanoparticles, further studies are required