

Comparison of Preparation Techniques of Cobalt Nano ferrites and their Characterization



Name: Shehzad Sohail
Reg. No. 2010-NUST-MS PhD-MS-E-14

**This work is submitted as a MS thesis in partial fulfillment of the requirement
for the degree of**

MS in Materials and Surface Engineering

**Supervisor: Meritorious Prof, Dr. Asghari Maqsood
(Sitara-e-Imtiaz)**

Department of Materials Engineering

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST), H-12

Islamabad, Pakistan

October, 2012

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

Declaration

I Shehzad Sohail, hereby declare that I have produced the work presented in this thesis, during the scheduled period of study. I also declare that I have not taken any material from any source except referred to wherever due. If a violation of HEC rules on research has occurred in this thesis, I shall be liable to punishable action under the plagiarism rules of the HEC.

Dated: 03-12-2012

Signature of the student

Shehzad Sohail

2010-NUST-MS PhD-MS-E-14

CERTIFICATE

This is to certify that the work in this dissertation has been carried out by Shehzad Sohail and completed under my supervision at Thermal Transport Laboratory, School of Chemical and Materials Engineering, National University of Sciences and Technology, Sector H-12, Islamabad, Pakistan.

Supervisor

Meritorious Professor Dr. AsghariMaqsood (SI)

Thermal Transport Laboratory

School of Chemical and Materials Engineering,
National University of Sciences and Technology,
Islamabad, Pakistan.

Submitted through

Prof. Dr. Mohammad Shahid

Head of Department of Material Engineering
School of Chemical and Materials Engineering,
National University of Sciences and Technology,
Sector H-12, Islamabad,
Pakistan.

DEDICATION

I dedicate my thesis to almighty **ALLAH** who is the only power in the universe and whose blessings made this work possible.

ACKNOWLEDGEMENTS

Firstly, I would like to express my deepest gratitude to my Supervisor, Prof. Dr. Asghari Maqsood (SI) for her kind guidance, support and help in every aspect throughout this duration. Her efforts in imparting the theoretical knowledge are greatly appreciated. I am deeply impressed by her everlasting passion and conscientious attitude to the research, which are invaluable to me and I should treasure forever.

I greatly acknowledge Dr. Muhammad Mujahid, Principal School of Chemical and Materials Engineering (SCME), and Dr. Mohammad Shahid, Head of Materials Engineering Department,

(SCME) NUST for providing me a platform to utilize my skills during the research work. They always helped me out whenever I needed their kind attention.

Most of the work presented in this thesis was done at Thermal Transport Laboratory of Department of Materials Engineering SCME. I also acknowledge PSF for using impedance analyzer through project No. Res/c-NUST phy.147 to measure the dielectric properties.

Sincere appreciation should be extended to all the faculty members, lab staff, non-technical staff and my fellow students. I specially thank to Dr. Muhammad Asghar, Mr. Allah Bakhsh, Mr. Zafer Iqbal, Mr. Khurram Shehzad, Mrs. Humera, Mrs. Erum and Mr. Zahid for their support in this period of my research.

I acknowledge School of Chemical and Materials Engineering (SCME), NUST, for the technical and financial assistance provided to me during my research. It was great honor for me to work in such a prestigious institute.

Last but not the least; I am most grateful to my father, mother, grand mother, sisters and brother-in-law for their sincere prayers and continuous support during the whole period.

Shehzad Sohail

ABSTRACT

Cobalt ferrite nanoparticles were successfully synthesized using sol-gel and the chemical co-precipitation methods. In sol-gel method nitrates of cobalt and iron was used. Citric acid was used as chelating agent and ammonia was used to maintain the pH at 7. Sample S1 was synthesized by sol-gel method. In chemical co-precipitation technique nitrates of cobalt and iron was used. Sodium hydroxide (NaOH) was used as a precipitant agent. Three different samples S2, S3 and S4 were synthesized using different molarity of the precipitant agent. All the samples were heat treated at 900⁰C.

Structural and morphological properties were investigated using XRD, SEM and EDS techniques. XRD results confirmed the formation of the spinal structure of the cobalt nanoferrites for each of the sample. Average crystallite size for sample S1, S2, S3 and S4 are 53.5nm, 21.5 nm, 35.5 nm and 35.5 nm respectively. SEM micrograph images confirmed the presence of

the nanostructured cobalt ferrite nanoparticles.EDS patterns showed the compositional purity of each of the sample. Calculated density is compared with the theoretical density. Electrical and dielectric properties were also measured for all the samples. Variation in the values of dielectric constant, dielectric loss and ac conductivity were measured in the range of frequencies from 100 Hz to 5 MHz. DC conductivity and ac conductivity was determined from this data. Results showed that cobalt ferrite synthesized by the sol-gel method had the greater value of resistivity and smaller values of dielectric constant and dielectric loss as compared to the sample prepared by the chemical co-precipitation method. So these materials can be used for the high frequency applications.

	<u>Contents</u>	Page No.
	Certificate	III
	Dedication	IV
	Acknowledgements	V
	Abstract	VI
	List of Figures	X
	List of Tables	XII
CHAPTER 1	Introduction and Literature Review	
1.1.	What is Nanotechnology	2
1.2.	Magnetism	3
1.2.1.	Types of magnetic materials	4

1.2.2. Diamagnetic materials	4
1.2.3. Paramagnetic materials	4
1.2.4. Ferromagnetic and Ferrimagnetic materials	5
1.2.5. Anti-ferromagnetic materials	5
1.3. Ferrites	6
1.3.1. Soft ferrites	6
1.3.2. Hard ferrites	7
1.4. Types of ferrites	7
1.4.1. Spinel ferrites	7
1.4.2. Garnet ferrites	9
1.4.3. Hexagonal ferrites	9
1.5. Cobalt ferrite	10
1.6. Objectives	12

CHAPTER 2 Synthesis and Characterization Techniques

2.1. Experimental techniques for the preparation of nano particles	14
2.1.1. Synthesis techniques of nanoparticles	15
2.1.2. Gas phase condensation method	15
2.1.3. Hydrothermal synthesis of nanoparticles	16
2.1.4. Combustion method	17
2.1.5. Spray pyrolysis method	17
2.1.6. Mechanochemical synthesis technique	18
2.1.7. Sol-gel synthesis technique	18
2.1.8. Chemical co-precipitation method	21
2.1.8.1 Rate of mixing of the reactants	23
2.1.8.2 Role of anion	23
2.1.8.3 Temperature effect	23
2.1.8.4 Effect of pH	23
2.1.8.5 Heating after co-precipitation	24
2.2. Characterization techniques	25

2.3. Structural characterization	25
2.3.1.X-ray diffraction characterization	25
2.3.2.Scanning electron microscopy (SEM)	26
2.3.3.Energy dispersive X-ray spectroscopy (EDS)	26
2.4.Electrical Properties	27
2.4.1Electrical resistivity measurement	27
2.4.2Dielectric properties measurement	27

CHAPTER 3 Synthesis of Cobalt Ferrite (CoFe₂O₄) Nanoparticles and Preparation of Samples

3.1. Synthesis of cobalt ferrite nanoparticles	30
3.2. Synthesis of cobalt ferrite nanoparticles by sol-gel method	30
3.3. Synthesis of cobalt ferrite nanoparticles by co-precipitation method	32

CHAPTER 4 Results and Discussions Cobalt Ferrite (CoFe₂O₄)

4.1 Characterization of cobalt ferrite (CoFe ₂ O ₄)	36
4.2 Structural characterization by XRD	36
4.3 Density measurements Porosity	40
4.4 Structural characterization by SEM and EDS	41
4.4.1.SEM and EDS results for sample S1	41
4.4.2.SEM and EDS results for sample S2	42
4.4.3.SEM and EDS results for sample S3	43
4.4.4.SEM and EDS results for sample S4	44
4.5.Electrical and dielectric properties of cobalt ferrite (CoFe ₂ O ₄)	45

CHAPTER 5 Conclusions and Future Work

5.1 Conclusions	50
5.2 Future Work	51
Reference	52

List of Figures

	Figure	Page #
Figure 1.1	Magnetic moment ordering (a) diamagnetic (b) paramagnetic (c)ferromagnetic (d) anti-ferromagnetic (e) ferrimagnetic	6
Figure 1.2	Spinal ferrite unit cells with octahedral and tetrahedral sites	9
Figure 2.1	Schematic of the nanoparticles synthesis approaches	14

Figure 2.2	Methods used for the preparation of particles by gas condensation method	15
Figure 2.3	Single crystal powder formations by hydrothermal process	16
Figure 2.4	The schematic of the spray pyrolysis method	18
Figure 2.5	Different products gained from the sol-gel process	20
Figure 2.6	Chemical co-precipitation steps	22
Figure 3.1	Schematic of the sol-gel process	32
Figure 3.2	Schematic of the chemical co-precipitation process	34
Figure 4.1	XRD pattern of the sample S1 prepared by the sol-gel method	38
Figure 4.2	XRD pattern of the sample S2 prepared by the chemical co-precipitation method	38
Figure 4.3	XRD pattern of the sample S3 prepared by the chemical co-precipitation method	49
Figure 4.4	XRD pattern of the sample S4 prepared by the chemical co-precipitation method	49
Figure 4.5	SEM images of the sample S1	41
Figure 4.6	EDS pattern of sample S1	41
Figure 4.7	SEM images of the sample S2	42
Figure 4.8	EDS pattern of sample S2	42
Figure 4.9	SEM images of the sample S3	43
Figure 4.10	EDS pattern of sample S3	43
Figure 4.11	SEM images of the sample S4	44
Figure 4.12	EDS pattern of sample S4	44
Figure 4.13	Graph between dielectric constant (ϵ') VS $\ln F$	46
Figure 4.14	Graph between dielectric loss (ϵ'') VS $\ln F$	46
Figure 4.15	Graph between ac conductivity σ_{ac} VS $\ln F$	47

List of Tables

Table		Page #
Table 1.1	Radius of some common metal ions used in the spinal ferrites.	8
Table 1.2	Different crystal types of ferrites.	10

Table 4.1	Results from XRD technique	40
Table 4.2	Density and porosity measurement	40
Table 4.3	Values of resistivity measured of each sample by dc source meter	47
Table 4.4	Values of ϵ' , ϵ'' , σ_{ac} and σ_{dc} at different frequencies	48

Comparison of Preparation Techniques of Cobalt Nano ferrites and their Characterization



**By
Shehzad Sohail**

**School of Chemical and Materials Engineering (SCME)
National University of Sciences and Technology (NUST)**

2012

CHAPTER 1

Introduction and Literature Review

1.1 What is Nanotechnology?

1.2 Magnetism

1.3 Ferrites

1.4 Types of ferrites

1.5 Cobalt ferrite

1.6 Objectives

1. Introduction

1.1. What is Nanotechnology?

Nanotechnology deals with manufacturing, devices, materials and structures with at least one dimension sized from 1 to 100 nanometers.

The word nanotechnology was used firstly in a talk in 1959 delivered by a physicist Richard Feynman. The developments of new microscopes in 1980 allow the researchers to see nanometers. One nanometer is the one-billionth of a meter. Today in laboratories of all over the world the basic research and development is happening on the nanotechnology. Nanotechnology is the hot area of research in all fields of sciences. For example in physics, chemistry, biological sciences and material sciences. In material sciences we are dealing mostly the clusters, nanoparticles, nanorods, nanowires, nano composites, nanowires and thin films.

Basically two approaches are there in the fabrication of nano materials Top down approach and bottom up approach. In top down approach the massive materials are converted into the smaller nanometer sized material. In bottom up approach small crystallites and atoms make the nanometer sized materials. Different methods and procedures are involved in the fabrication of nano sized materials.

A number of phenomenon take place when we move from larger sizes to reduced one. This effect on the properties of materials does not much visible by moving from macro to micro dimensions of the materials. But when size is reduced to nanometers scale an abrupt change is observed in the properties of the material.

The physical properties like electrical, mechanical, optical, etc. changes when the size of material enters into the nanometer range. One reason of change in the properties at nanoscale is the increase in the surface area to volume ratio. The change in the mechanical, catalytic and thermal properties is observed due to increase in the surface area to volume ratio at the nano scale. Some materials which are opaque at macro-scale become transparent at nano scale as copper. Some materials which are stable at macro-scale become combustible at nano scale as aluminum. Some materials which are insoluble at macro-scale become soluble at nano scale as gold. Some materials which are inert at macro-scale become catalyst at nano scale [1].

When the particle size reduced to nanometer scale some defects are generated in the constituting atoms. The great change in the physical, chemical and optical properties

is due to the small grain size, large number of grain boundary junctions and interfaces, pores and different lattice defects. All these are produced due to size reduction [2, 3].

The change in the properties of materials at nano scale has remarkable applications and opened a new world for the scientists and researchers. Nano materials are justifying their place with their uses in almost all the fields of science and engineering.

Some of the applications of nano materials in different fields are mentioned here.

As the oxide nanoparticles mixed in a polymer matrix results into a composite structure.

Nanocomposites have so many industrial applications. Nanocomposites are lightweight so they have replaced the conventional heavy metals in the vehicles. Due to lightweight the vehicles becomes speedy, fuel efficient, and more resistive against corrosion. Nano composites are also using in construction industry, buildings and so many home appliances [4].

The gas leaking sensors are of great importance and the nanomaterial based gas sensors have improved performance. This is due to the higher values of surface to volume ratio.

Nanotechnology is also having a great importance in the medical field. For example DNA attached with gold nanoparticles used for the detection of genetic sequence. Drug delivery into the specific cell is also possible by using the nanoparticles. Iron nanoparticles are being used for the cancer treatment. Allergy can be interrupted by the Buckyballs [5].

Low energy consumption displays can be made by using carbon nanotubes. The fields which are giving space to the nanotechnology are textiles, cosmetics, agriculture, sports, optics, household, food, vehicle manufacturing. So the nanotechnology is progressing in every field of life.

1.2 Magnetism

The property of a material when the material is subjected to the applied magnetic field the material will respond called magnetism.

Some materials are attracted by the magnetic fields some materials are repelled by the applied magnetic fields and some are unaffected by the external magnetic field.

Magnetic materials can be classified as under .There are two important quantities which relate B(magnetic flux density) and M (magnetism) to H(magnetizing force). the magnetic susceptibility χ and the magnetic permeability μ [6].

$$\chi = M / H \quad (1.1)$$

$$\mu = B / H \quad (1.2)$$

1.2.1 Types of magnetic materials

The source of magnetism in the materials is the motion of electron. Electrons have two types of motions.

a) - Motion of electrons in the orbit around the nucleus called orbital motion of electrons.

b) - Motion of electrons around their own orbit called spin motion of electrons.

The motion of electrons plays an important role in the classification of magnetic materials. Magnetic materials can be classified as under.

1.2.2 Diamagnetic materials

These are the materials which oppose the external magnetic field. Diamagnetic materials have not any unpaired electrons. Diamagnetic material describes negative magnetic susceptibility. Diamagnetic materials include wood, water, some plastics, gold, bismuth, copper. The magnetic domains of the diamagnetic materials can be shown as in fig 1.1 (a)

1.2.3 Paramagnetic materials

In the presence of external magnetic field the materials which attract towards the applied field are called paramagnetic materials. In the absence of external magnetic field the dipole moments are not aligned. So no net magnetization is there but when the external field is applied there is a net magnetization [7]. These have positive but very low value of magnetic susceptibility

Cesium, Aluminum, Sodium, and tungsten are the examples of Paramagnetic materials. The magnetic domains of the paramagnetic materials can be shown as in

fig 1.1 (b)

1.2.4 Ferromagnetic and Ferrimagnetic materials

In the absence of external magnetic field these materials have a permanent magnetic moment. In ferromagnetic materials all the magnetic moments aligned and results into large value of magnetization. In ferrimagnetic materials opposing magnetic moments are also there but the magnetizations remain there. These have also a large value of permanent magnetization [7]. These materials also have positive value of magnetic susceptibility. Iron, nickel, and cobalt are the examples of ferromagnetic materials. Ferrimagnetic materials are electrically insulators. Magnetic garnets and ferrites are the example of ferrimagnetic materials. The magnetic domains of the ferromagnetic materials can be shown as in fig 1.1 (c) .The magnetic domains of the ferrimagnetic materials can be shown as in fig 1.1 (e)

1.2.5 Anti-ferromagnetic materials

In the anti-ferromagnetic materials the magnetic moments of molecules or atoms is directly related to the spins of electrons with neighboring spin of electrons in opposite direction.

Anti-ferromagnetic materials have the ordered magnetism like ferromagnetic materials and ferrimagnetic materials. Anti-ferromagnetic behavior of materials is observed below a critical temperature called Neel temperature. Above the Neel temperature anti-ferromagnetic materials may convert into the paramagnetic materials [8]. The examples of the anti-ferromagnetic materials are chromium, iron manganese, and nickel oxide. The magnetic domains of the anti-ferromagnetic materials can be shown as in fig 1.1 (d)

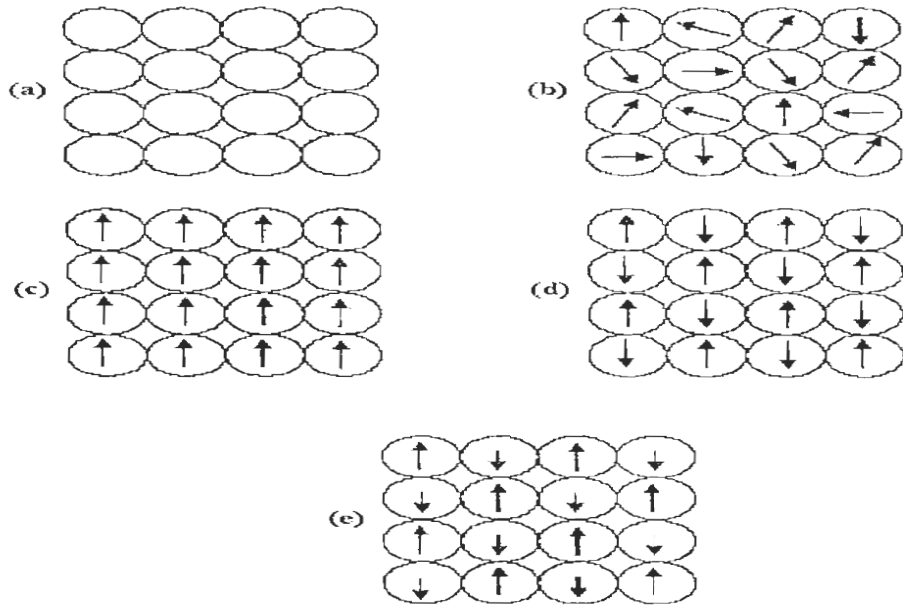


Fig 1.1 magnetic moment ordering (a) diamagnetic (b) paramagnetic (c) ferromagnetic (d) anti-ferromagnetic (e) ferromagnetic [8]

1.3 Ferrites

Ferrites are the most important ferrimagnetic materials. Iron oxide (Fe_2O_3) is the principal component in the ferrites[9]. Due to presence of Ferrimagnetic oxides ferrites are insulating materials [10]. Ferrites are magnetic materials which are used to make transformer cores, permanent magnets and in other so many applications. These are mostly used in the high frequency application as they restrict the production of eddy currents because of high resistivity. The value of electrical resistivity of ferrites is very high. There are two structural symmetries of ferrites which are based upon the charge and mass of the metal ions. One is the cubical other is hexagonal structure [11]. There are two types of ferrites based on the hysteresis losses.

1.3.1 Soft ferrites

The ferrites which have low coercivity are known as soft ferrites. The materials which have the low value of energy dissipation in magnetization or demagnetization have low value of coercivity. They appear dark black or gray. These are very hard

and brittle. Soft ferrites have high value of resistivity these are used to prevent the energy losses like in the cores of transformers and inductors. Manganese zinc ferrite and nickel zinc ferrite are the examples of soft ferrites.

1.3.2 Hard ferrites

Hard ferrites are known as ceramic magnets. Hard ferrites have the high value of coercivity. High coercivity means the material take large time to demagnetize. The magnetic permeability of the hard ferrites is very high. Hard ferrites are made of iron, strontium and barium oxides. Hard ferrites are very cheap in cost. As the raw material is easily available to make hard ferrites. These are being used excessively in the house hold things due to their low cost. Some of the important hard ferrites are ferrite, strontium ferrite and cobalt ferrite.

1.4 Types of ferrites

There are three types of ferrites depends upon the structure of the ferrites. We can categories ferrites as under [12].

1.4.1 Spinal ferrites

1.4.2 Garnet ferrites

1.4.3 Hexagonal ferrites

1.4.1 Spinel Ferrites

Spinel ferrites have the general formula $MF_e_2O_4$. Here M is a divalent cation. Cobalt (Co^{+2}), Copper (Cu^{+2}), Zinc (Zn^{+2}) and Nickel (Ni^{+2}) are the examples of divalent cations. Spinel ferrites have the simpler structure as compared to the other ferrite types. The unit cell of spinel lattice is composed of 32Oxygen ions. The anions are arranged in a close-packed structure (FCC). There are two types of space sites between the anions .we refer in the fig as A and B sites.

(A). Tetrahedral sites

(B). Octahedral sites

Tetrahedral site is the site which is surrounded by the 4 oxygen atoms. A spinel structure acquires 64 tetrahedral sites. The cations occupy 8 of the tetrahedral sites out of 64. The tetrahedral position is shown in the fig (1.2).

Octahedral site is surrounded by the 6 oxygen atoms. There are 32 octahedral sites in

the spinel ferrite structure. 16 octahedral sites are occupied by anions. The tetrahedral position is shown in the fig (1.2).

The occupation of the A and B sites result into the electrically neutral structure of spinel ferrite [11].

Table 1 Radii of some common metal ions used in the spinel ferrites[11].

Ion	Ionic radius Å
Fe^{2+}	0.83
Fe^{3+}	0.67
Co^{2+}	0.82
Zn^{2+}	0.74
Ni^{2+}	0.78
Mn^{3+}	0.70

Two types of spinel structure are there:

(a) Normal spinel

(b) Inverse spinel

In normal ferrites all trivalent metal ions are present at the B sites and all the divalent metal ions occupy the A sites in the crystal structure.

In inverse spinel ferrites trivalent ions occupy both the A and B sites and all divalent metal ions occupy the B sites in the crystal structure.

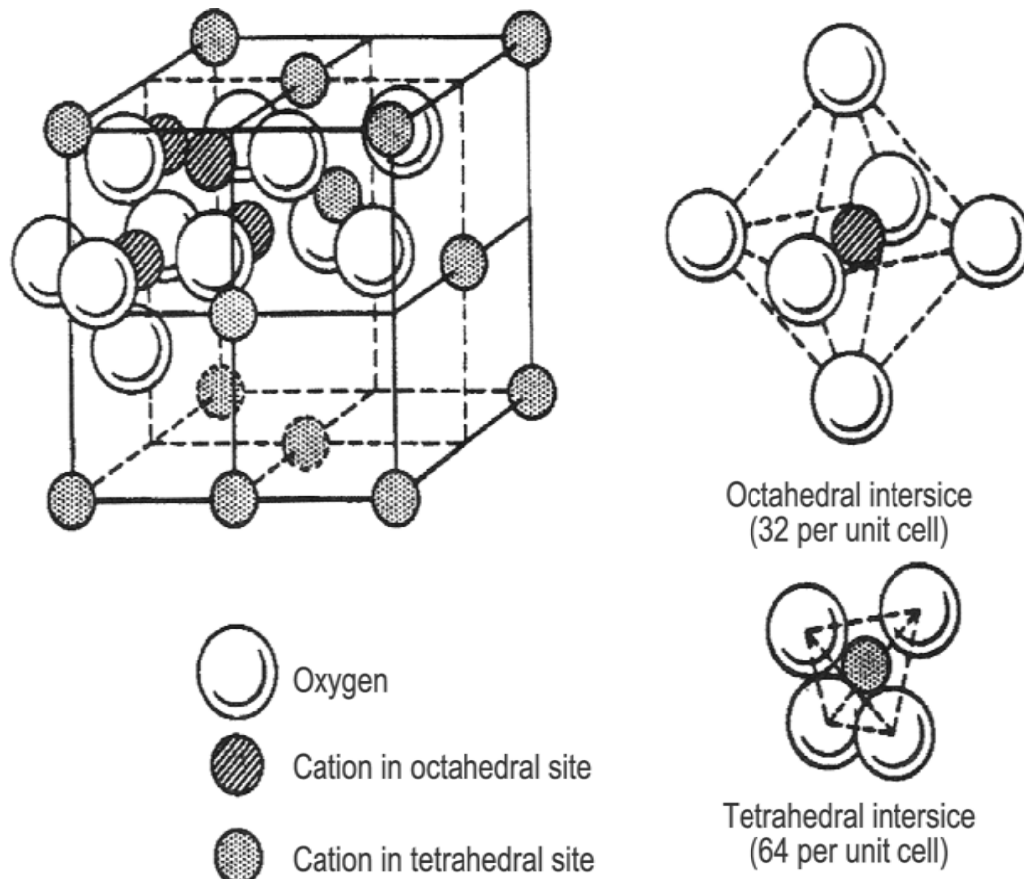


Fig 1.2 Spinel ferrite unit cell with octahedral and tetrahedral sites [13].

1.4.2 Garnet ferrites

Giller and Gilleo discover the Garnets in 1957. These have cubic structure with the general formula $M_3Fe_5O_{12}$. Where M is the rare earth trivalent ion. Y, Gd, and Dy are the examples of the rare earth trivalent ions. Garnet ferrites are magnetically hard materials.

1.4.3 Hexagonal ferrites

Hexagonal ferrites have the general formula $MFe_{12}O_{19}$. Here M can be cobalt, strontium, barium or the combination of these. Hexagonal ferrites are using as permanent magnet as it have a high value of coercivity [10].

Hexagonal structure is similar to the spinal structure. The metal ions occupy three different sites in the structure. These sites are octahedral, tetrahedral and trigonal. These magnetic materials are widely used in every field as in the magnetic recording

devices, in loud speakers, in microwave applications and as fridge magnets.

A brief overview of different crystal structured ferrites and there examples are listed in the table 2

Table 2 Different crystal types of ferrites [10].

Type	Structure	General Formula	Example
Spinel	Cubic	$M^{II}Fe_2O_4$	$M^{II}=Fe, Cd, Co, Mg, Ni \text{ and } Zn$
Garnet	Cubic	$M^{III}_3Fe_2O_{12}$	$M^{III}=Y, Sm, Eu, Gd, Tb, \text{ and } Lu$
Magnetoplumbite	Hexagonal	$M^{II}Fe_{12}O_{19}$	$M^{II}=Ba, Sr$

1.5 Cobalt ferrite

Cobalt ferrite is a very important material. It has captured the attention of the researchers due to so many useful applications in magnetic fluids, magnetic recording devices, high resistivity and many more[14, 15].

Cobalt ferrite ($CoFe_2O_4$) has good chemical stability and excellent mechanical hardness [16].

Cobalt ferrites are the cubic ferrites. These have the inverse spinel structure. Where Fe^{+3} is located at A and B sites and Co^{+2} is located at B site. Cobalt ferrite has the anisotropy constant value in the range form 1.8 to 3×10^6 erg/cm³. [17].

The use of the cobalt ferrite in the magnetic recording devices must posses the high value of coercivity. High value of coercivity depends on the particle size of the material. The particle size near the critical size of the particle has the larger value of coercivity. The critical size is equal to the size of single domain. Co-precipitation and sol-gel processes are widely used for the synthesis of cobalt ferrite nanoparticles. Fe (III) and Fe (II) salts are used for the synthesis of the cobalt ferrite nanoparticles [18, 19].

Blaskov in (1996) produced the cobalt ferrite by using co-precipitation of Iron and cobalt solutions. The calcination at 598 K is performed. The cobalt ferrite particles with diameter $50 \pm 5 \text{ \AA}$ produced. XRD patterns showed that the lattice parameter is

8.20 Å and structure is cubic spinel. Cobalt ferrite (CoFe_2O_4) was prepared by the Li (2006) [20].

The particle size obtained by Li was 10 to 15 nm. Moumen in 1995 produced the nanoparticles with diameter of 5nm [21]. In 1996 Pialli produces the Cobalt ferrite (CoFe_2O_4) with diameter less than 50 nm [22].

The electrical, dielectric properties of the cobalt ferrite are of great concern. There are so many applications related to the electrical and dielectric properties of the ferrites. A lot of work has been done on these properties. Dielectric constant, dielectric loss, ac and dc electrical resistivity are very dependent on the crystal structure, grain size of the cobalt ferrite. The crystal structure and grain size is depends on the process by which the material is formed.

AC conductivity (σ_{ac}) increases by increasing the frequency. AC conductivity increases up to the 1 kHz and on further increase of frequency conductivity decreases. The decrease of ac conductivity is due to the applied field frequency can not leads the hopping frequency between the ions [23]. AC conductivity (σ_{ac}) also increases by increasing the temperature.

The dielectric loss is due to the imperfection and impurities in the crystal lattice [24].

Dielectric constant (ϵ') also increases on increasing the frequency. Up to 10 kHz the dielectric constant increases. On further increase in frequency the dielectric constant decreases. The reason for the change in dielectric constant with the frequency is that the ferrites conversion from ferromagnetic to paramagnetic on changing the frequencies. The dielectric constant (ϵ') also changes with changing the temperature [25].

1.6 Objectives

The objectives of this thesis are,

1. Synthesis of cobalt-ferrite nanoparticles with the help of sol-gel and co-precipitation methods.
2. The comparative study of their structure with the help of XRD and SEM
3. The Comparative study of their electrical properties.
4. The Comparative study of their dielectric properties.

Chapter 2

Synthesis and Characterization Techniques

2.1 Experimental techniques for the preparation of Nano particles

2.2 Structural Characterization

2.3 Electrical Properties

2.1 Experimental techniques for the preparation of nano particles

So many methods are used for the synthesis of the nano particles some of them are included here.

Two types of the approaches are there basically for the synthesis of the nanoparticles.

(a) Top down approach

(b) Bottom up approach

In top down approach we start from the bulk and moves toward the nano sizes. Top down approach include Lithography, Mechanical attrition, and etching.

In bottom up approach we start with atom, molecules or clusters which then converted into the crystallites by nucleation and then finally give the particles by the growth process. The bottom up approach includes powder aerosol compaction and the chemical methods.

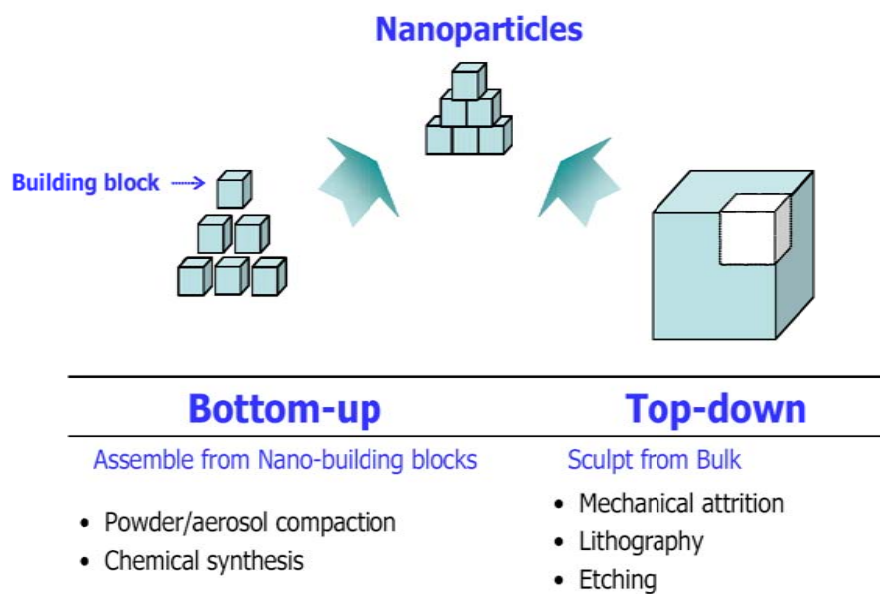


Figure 2.1 a schematic of the nanoparticles synthesis approaches

2.1.1 Synthesis techniques of nanoparticles

Cobalt ferrites can be synthesized by different techniques. Some of them are discussed here. The ferrites particles prepared by different methods possess different structural, electrical and dielectric properties. As the different techniques involve different raw materials and variation of temperature applied so the products have different properties. The nanoparticles may be generated by the condensation of gases or crushing down the solids into the micro and nano level particles. The particles may be generated with the help of chemical methods.

2.1.2 Gas phase condensation method

The nanoparticles can be produced with the help of condensation of the gas molecules. This is generally obtained from aerosol processes [26]. Particles of the nanometer size can be formed with the help of gas phase condensation method. The particles form has size less then 100 nm. In this method gas molecules are formed with the help of chemical or physical reaction in the aerosol reactor [27]. The precursor molecules form nuclei as a result of reaction in the vapor phase. Then the tiny nuclei grow and form the particles of nano size particles. This method can be used at laboratories as well as at industrial scale to get nanoparticles. The nanoparticles obtained by this method mostly have the same properties as that of the precursor molecules. Different methods witch are using the gas condensation method can be listed in the diagram.

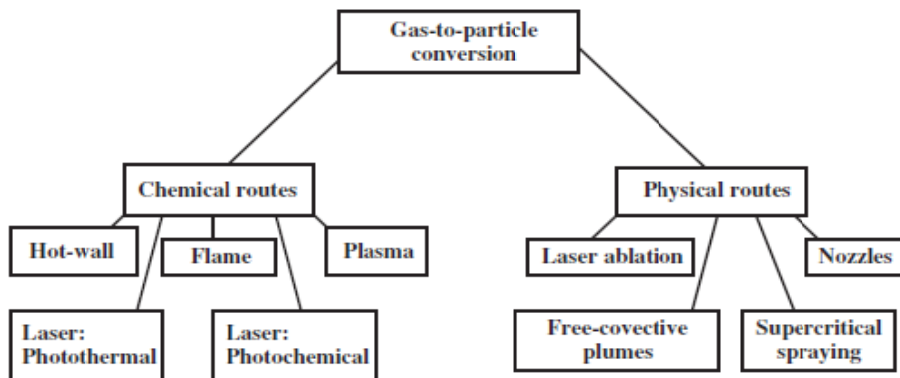


Figure 2.2 Methods used for the preparation of particles by gas condensation method [28].

2.1.3 Hydrothermal synthesis of nanoparticles

It is a method used to create single crystals or particles. The synthesis of the single crystal depends on the materials under high pressure in the water. The whole process is carried out into a vessel known as autoclave. For the growth of the crystals a temperature gradient is maintained inside the autoclave. The critical value of temperature and pressure used in autoclaves are 374 degree centigrade and 15 MPa respectively. With the help of this method single crystal of desired phase, excellent morphology, purity, and powder reactivity can be obtain [29].

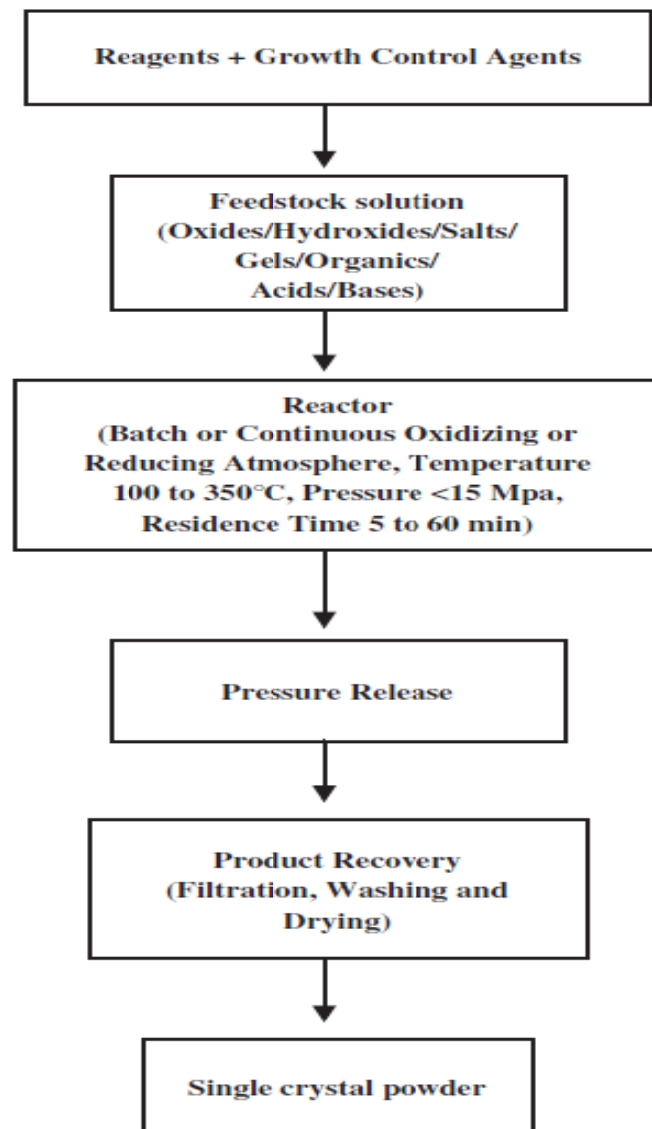


Figure 2.3 Single crystal powder formations by hydrothermal process [32].

In hydrothermal synthesis for the preparation of the ceramic oxides and the fine

nanoparticles water under high temperature and pressure is used [30]. The single crystal is formed in the autoclaves do not require annealing. The final product formed at a low temperature this is the main advantage of the hydrothermal process.

autoclaves are very expensive and the growth of the crystal inside the autoclave can not be seen this is the main disadvantage of the hydrothermal process[31]. The whole process from sol formation to the final product can be expressed as in the block diagram.

2.1.4 Combination method

Combination method is an interesting method used for the preparation of nanoparticles. In this technique an exothermic reaction is taken place to cross the energy barrier to activate the reaction [33]. This method involves a reducing agent called fuel and an oxidizing agent. This combination of precursor is called redox mixture. The redox mixture burn in a while and give the product. Due to production of large value of gas the particles break down into smaller one. This is a very fast method to prepare nanoparticles. The main disadvantage of this process is that we can not get the desired size of the particles. It is very difficult to control the size of the particles.

2.1.5 Spray pyrolysis method

This is a power full technique to form the homogeneous and ultra fine nanoparticles [34]. In this process the metal ions are dissolved in the solution the solution is called the precursor solution or sol. The Sol is then converted into the tiny liquid particles with the help of an atomizer. The droplets are not of the same size when they are released from the nozzle. The sprayed liquid particles are the suspended in the aerosol generator. Then the suspended particles are go throw from a furnace. Where the droplets heat treated and converted into the final product. We can not carry it at industrial scale due to high cost processing. The shape and size of final product is very difficult to control in this process.

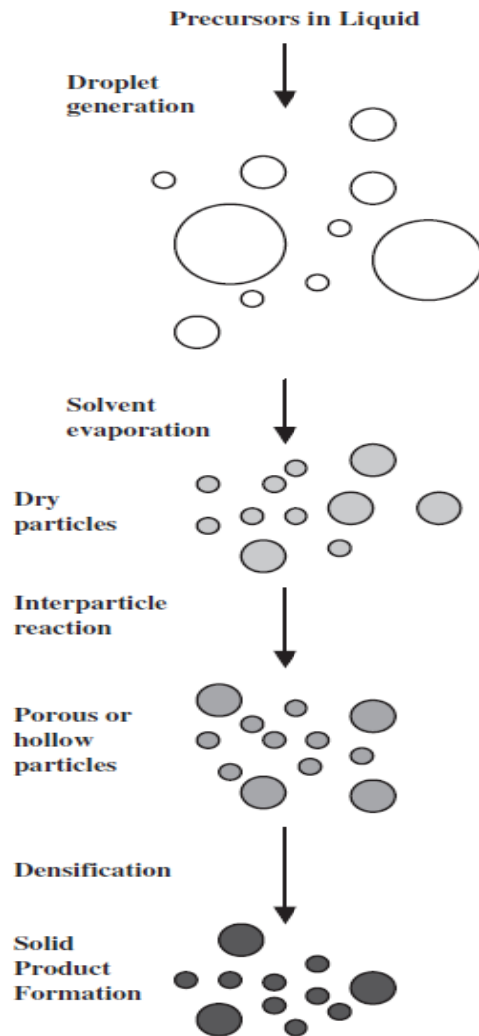


Figure 2.4 the schematic of the spray pyrolysis method [35].

2.1.6 Mechanochemical synthesis technique

For the low cost synthesis of the nanoparticles mechanical milling technique is being used. This is a very old technique. In simple milling the bulk is converted into the desired product. But in mechanochemical synthesis a continuous milling of the reactive powder is involved. The milling apparatus must have the high milling rate, high frequency, good impact velocity. After a reasonable time of milling the size of the reactive components decreases and their surface area increases. So the final product is produced at lower temperature. A variety of the nanoparticles can be made by using this technique [36].

2.1.7 Sol Gel Synthesis technique

Sol Gel is a very important wet chemical technique for the synthesis of the so many use full products. The products such as aerogel, xerogel, thin films, nanoparticles. Our focus is on the synthesis of the nanoparticles. In sol-gel method the porosity and surface area is controllable [37].

We divide the process in following steps

- Hydrolysis
- Condensation
- Gelation
- Aging
- Drying
- Densification

The sol can be formed by dissolving the organic, inorganic salts or the metal alkoxide in a solvent. When the sol is drying it results into the formation of a polymeric network known as gel.

In sol-gel process the behavior of the sol the properties of the gel and the method adopted for the formation of the final product are the key factors which control the properties of the final product [38]. The main advantage of the sol-gel method is the low temperature requirement for the synthesis of the final product. This technique is very applicable for the synthesis of the desired phase of the metal oxides.

Sol-gel process is may be of two types.

- Aqueous sol-gel
- Non-aqueous sol-gel

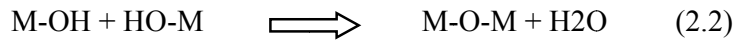
In aqueous sol-gel method the hydrolysis and condensation of the metal alkoxide gives the M-O-M. In addition condensation may release water or alcohol depends on the reactants.

The chemical equations which show the aqua sol-gel hydrolysis and condensation reactions are given below.

Hydrolysis



Condensation with water release



Condensation with alcohol release



Scheme 2 Hydrolysis and condensation reactions in the aqueous sol-gel method

In Aqueous sol-gel the water gives the required oxygen for the synthesis of oxides but in the non Aquas the solvent is alcohols, ethers or ketone. So the required oxygen is provided by these solvents.

In sol-gel process mostly the hydrolysis rate is faster as compared to condensation. When the pH of the sol is in between 7-9 the condensation rate is faster then the hydrolysis rate. When the condensation rate is higher the gel type structure is formed [39]. The whole process of the sol-gel is shown in the figure.

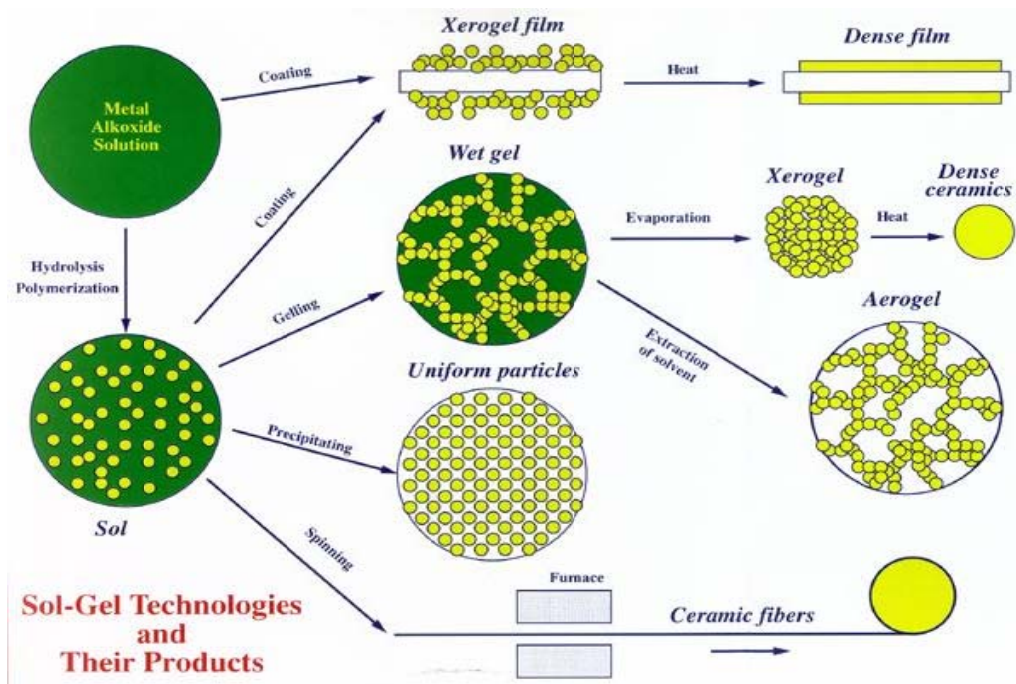


Figure 2.5 different products gained from the sol-gel process [40].

Main advantages of the sol-gel process are given by [41].

- Low synthesis temperature
- Excellent mixing of raw materials
- Better homogeneity and purity from the raw materials.
- Good control of shape, size and properties of final product.
- A variety of products can be formed by using this technique.
- It is possible to create organic materials, inorganic and hybrid materials.
- The material structure can be designed by using this technique.
- No special apparatus is required in this process.
- Good control over micro-structure of the final product.

Effect of variation in the different parameters on the chemistry of the process. Some of the important variables in the sol-gel process are given below [42].

- pH of the solution
- Water to metal alkoxide ratio
- Metal loading
- Gelation temperature
- Solvent remove
- Pretreatment conditions

The gel formation in the process depends on the number of water mole added in the solution. When the ratio of water to the alkoxide increases the time require for gel formation also increases. The time of gel formation also increases when the pH of the solution is low. The synthesis of the metal oxides is normally performed at normal value of pH. Under basic condition the particle size is 1 nm, under neutral condition particle size varies from 2 to 20 nm range. Under acidic condition particle size is 3 nm in the sol and gel [43]. The drying process is an important step in the formation of final product. Different types of drying processes can be used mostly thermal drying is used in the labs. The time and temperature values have great influence on the properties of the product.

2.1.8 Chemical co-precipitation method

Co-precipitation method is a very wonderful method to create the fine particles of nano sizes. It is very fine procedure to obtain ferrites with the help of co-precipitation method. Because the ferrites obtained by this method are pure and homogeneous in their chemistry,

Under fine control of pH by adding NaOH the various salts like sulphates, nitrates, and chlorides results into the oxide nanoparticles in a co-precipitation process [44]. In co-precipitation process the particle size is depend on the pH of the starting precursors. Particle size also depends on the molarity of the chemicals. Concentration of the chemicals affects the transport and chemical rates. The reaction rate and the impurities affect the crystallinity of the particles. Particle shape size is affected by some factors growth rate, nucleation and super saturation. At high super saturation the particle size is small and at high super saturation the size of particle becomes small. Mostly NaOH is used as precipitating agent. A reasonable value of pH and temperature is required for the precipitation purpose. The whole process for the co-precipitation can be shown in the figure below.

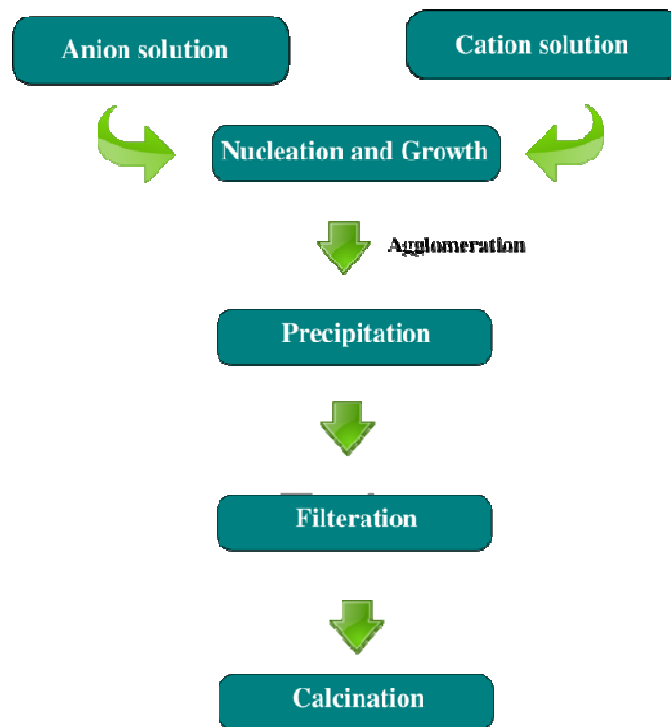


Figure 2.6 Chemical co-precipitation steps [45].

In co-precipitation process some parameters have great influence on the precipitate formation and the size and shape of the particles formed.

Some parameters and their influence on the co-precipitation process can be described

as under.

2.1.8.1 Rate of mixing of the reactants

2.1.8.2 Role of anion

2.1.8.3 Temperature effect

2.1.8.4 Effect o PH

2.1.8.5 Heating after co-precipitation

2.1.8.1 Rate of mixing of the reactants

The rate of mixing greatly influenced the size of the particles. Nucleation and growth are the two important processes in the co-precipitation process. Small size particles are formed when the growth rate is slow and the nucleation rate is higher then the growth rate. In the same way the large particles are formed when nucleation rate is low as compared to the growth rate. In first case the rate of mixing of the precursors is very high and in the second case rate of mixing is low.

Slow mixing gives the particles of homogeneous chemistry.

2.1.8.2 Role of anion

The properties of the particles formed in the co-precipitation process is also depends in the types of anions used. Anions may be in the form of metal ion solutions of in the form of salts. For good results the use of the metal salts are recommended. The metal salts are may be the sulphates, nitrates or chlorides.

2.1.8.3 Temperature effect

Different metals have the different values of activation energy for the ferrites formation. The activation energy is obtained from the heat given to the reactants.

For the formation of cobalt ferrites use mostly use the reaction temperature in the range 70-100 centigrade.

2.1.8.4 Effect of pH

PH plays an important role in the synthesis of controlled size and shape particles. At low values of pH the growth of the particles is no significant. On increasing the value of the pH the growth rate of the particle yield is high enough. Increase in the pH value decreases the time required for the synthesis of the product. In our case of

Cobalt ferrites the pH range is 11-12.

2.1.8.5 Heating after co-precipitation

When the co-precipitation process is completed for the formation of the required phase annealing is required. The level and duration of heating is impotent in the sense of the required size and shape of the particles depends on these factors.

Chemical co-precipitation process has many advantages over other synthesis techniques [46].

- Mono-dispersed and homogeneous particles formation
- Rapid and simple preparation of particles
- Particle shape and size are easily controllable
- Particle composition is also controllable

2.2 Characterization techniques

2.3 Structural Characterization

2.3.1 X-ray diffraction characterization

X-ray diffraction technique is very important technique. With the help of this technique critical features like material composition, chemical bonding, molecule interaction, crystallite size and crystal structure can be measured. This technique has much importance in the field of nanoparticles study [47].

When the crystallite size is in the nanometer range the diffraction peaks becomes broaden. A collimated beam of wavelength 1.5406Å of X-ray is fallen on the specimen. The incident beam is then scatter in the way that some of the rays interfere in the constructive way and some in the destructive way. Constructive interference depends on the condition stated by Bragg [48].

$$N\lambda = 2d \sin\theta \quad (2.4)$$

Where (λ) is the wavelength of the X-radiation. (d) is the spacing between two atomic planes and (n) is the number of planes. Where (θ) is the angle of diffraction. (d_{hkl}) the inter-planer distance can calculated as below.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2.5)$$

This is the case when $a=b=c$.

Sample can be easily identified by comparing the X-ray diffraction data with ICDD files. ICDD means international center for diffraction data.

The crystallite size can be measure by using the Scherrer formula. Scherrer formula can be written as.

$$D = 0.9 \lambda / \beta \cos\theta \quad (2.6)$$

Where (λ) is the wavelength of the x-ray beam used, β is the full wave half maximum (FWHM). (FWHM) is equal to the angular width. D is the particle size. Thermal and elastic properties can be obtained by recording the X-ray patrons as a function of pressure and temperature.

2.3.2 Scanning electron microscopy (SEM)

It is the excellent techniques used for the characterization of the nanoparticles. We can find out the morphology and micro-structure of the nanomaterial with the help of this technique. It can measure the nanomaterial of few nanometer lengths. The main principle of the SEM is that an electron beam moves over the sample which produces the secondary electrons of low energy and back scattered high energy electrons. The secondary electrons are responsible for the topographical information obtained from a surface. With the help of the back scattered electrons we get the information about the chemical composition of the sample [49, 50]. The resolution of the SEM is up to 1 nm.

2.3.3 Energy Dispersive X-ray spectroscopy (EDS)

EDS is a device which is attached to the SEM. It is mainly used to find out the chemical composition of the sample. In the SEM very high energy electrons falls on the surface of the material and then due to high energy of these electrons the characteristic x-rays emitted out. These x-rays are used in the EDS. The x-rays are plotted on the graph in the form of distinct peaks. These peaks are then compared to the data available which gives the composition of the material exposed. EDS is very important technique in the sense that it is used to find out the composition of the nanoparticles. Cation mixing can also be finding out by using the EDS.

2.4 Electrical Properties

2.4.1 Electrical resistivity measurement

Electrical resistivity can be measured by using DC source meter. The principle of this meter is that the sample is considered as a resistance. The voltage is applied at the ends of the sample. The current is measured corresponding to the voltage applied. According to the Ohm's law

$$R = \frac{\rho l}{A} \quad (2.7)$$

Where (R) is the resistance of the material, l is the length of the sample, and (A) is the area of the sample and (ρ) the resistivity of the material. So from this relation the resistivity of the sample can be found out. The conductivity is the reciprocal of the resistivity. Conductivity can be written as (σ) [51].

The conductivity, resistivity and the mobility can be easily measured by using the two probe apparatus.

2.4.2 Dielectric properties measurement

The dielectric properties are very important for the ferrites. Especially when the materials are used for the memory devices. When the particle size is in the nanometer range the dielectric properties becomes so important. The ferrites are the excellent dielectric materials. These have a range of applications from radio to micro wave frequency. It is important to study the ferrites dielectric properties at different range of the frequency. The methods of preparation of the ferrites have great influence on the dielectric properties. We used the LCR meter to study the dielectric properties. The dielectric constant ϵ is measured at room temperature from 100 Hz to MHz. Accurate measurement of the dielectric constant is very important to explain different theories.[52, 53, 54]. The dielectric constant can be finding out by using the relation given as [53].

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (2.8)$$

Where (A) is the area of the pellet, d is the thickness of pellet; (C) is the capacitance and (ϵ_0) is the permittivity of free space. The ac conductivity can be formulated as [53].

$$\sigma_{ac} = \frac{J}{E} \quad (2.9)$$

Here (E) is the electric field density and (J) is the electric current density. By using the substituted values the ac conductivity can be formulated as,

$$\sigma_{ac} = \frac{J}{E} = \epsilon j \omega \quad (2.10)$$

ϵ is the complex function can be defined as,

$$\epsilon^* \approx (\epsilon' - j\epsilon'') \quad (2.11)$$

The dissipation or loss factor can be written as,

$$\tan\delta = \epsilon'' / \epsilon' \quad (2.12)$$

Now the final relation to find out the ac conductivity (σ_{ac}) can be written as [55].

$$\sigma_{ac} = \omega \epsilon' \epsilon_0 \tan\delta \quad (2.13)$$

$\tan\delta$ is the loss factor and (f) is the frequency applied.

Chapter 3

Synthesis of Cobalt Ferrite (CoFe_2O_4) Nanoparticles and Preparation of Samples

3.1 Synthesis of Cobalt ferrite nanoparticles

3.2 Synthesis of Cobalt ferrite nanoparticles by Sol-gel method

3.3 Synthesis of Cobalt ferrite nanoparticles by Co-precipitation method

3.1 Synthesis of cobalt ferrite nanoparticles

Cobalt ferrites can be synthesis by different methods. The different methods include

- Gas phase condensation method
- Hydrothermal synthesis of nanoparticles
- Combination method
- Spray pyrolysis method
- Chemical co-precipitation method
- Sol-gel method

Different synthesis methods have different advantages and disadvantages. Sol-gel and chemical co-precipitation methods have several advantages over the other synthesis techniques. So we used these two techniques for the synthesis of the cobalt ferrite nanoparticles.

3.2 Synthesis of cobalt ferrite nanoparticles by sol-gel method

Sol-gel method is a very useful and reliable synthesis technique. The powder obtained from this this process is homogeneous and can be regain. The instruments used for the synthesis process are listed below.

- Stirring Machine
- Magnetic stirrer
- Glass jars
- pH meter
- Mortar and pestle
- Electric Oven
- Tube Furnace

The chemicals used for the synthesis are listed below.

- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.1 M
- $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.2 M

- Citric acid (Chelating agent)
- Deionized water

Firstly 2.91 gm cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) is dissolved into 100 ml of deionized water and 8.08 gm Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) is dissolved into 100 ml deionized water. In this way .1 M solution of cobalt nitrate and .2 M solution of iron nitrate is obtained. 18.9 gm citric acid is dissolved into the 100 ml deionized water. These three solutions are put separately on the stirring machines. The magnetic stirring is continued for 30 mins at 45°C . Then the solutions of cobalt nitrate, iron nitrate and chelating agent are mixed in a large glass jar. Magnetic stirring is continued at higher temperature about 90°C . Then 33 % ammonia is added drop wise to maintain the pH of the solution at 7. Heating, stirring and addition of ammonia continued until the sol is not converted into the gel. When the gel is formed the stirring rate is slowed down and addition of ammonia is stopped. The heating is continued at the same rate. After a time span of 10 mins the gel is burned out this phenomenon is called auto combustion. The auto combustion process results into the formation of the cobalt ferrite powder. The whole process can be shown in the block diagram below.

The Cobalt ferrite (CoFe_2O_4) powder is the put into the electric oven for drying at 100°C . After drying the powder the pellets are formed. The dried powder is then mixed homogenously with the help of mortar and pestle. The dried powder is pored into a steel die and the pressed the piston by a load of 4 tons. In this way disk shape pellets of cobalt ferrite are formed. For the required phase formation heat treatment of the pallets is necessary. The pellets are placed into a tube furnace for heat treatment. The temperature of the tube furnace is adjusted at 900°C for 4 hours. After 4 hours the pellets are furnace cooled and then placed out side the furnace. Besides the pellets the cobalt ferrite powder is also heat treated into the tube furnace. Sol-gel process is very important because of its so many advantages [56]. The pellets are then characterized by XRD, EDS and SEM characterization techniques. Electrical and dielectric properties are also measured.

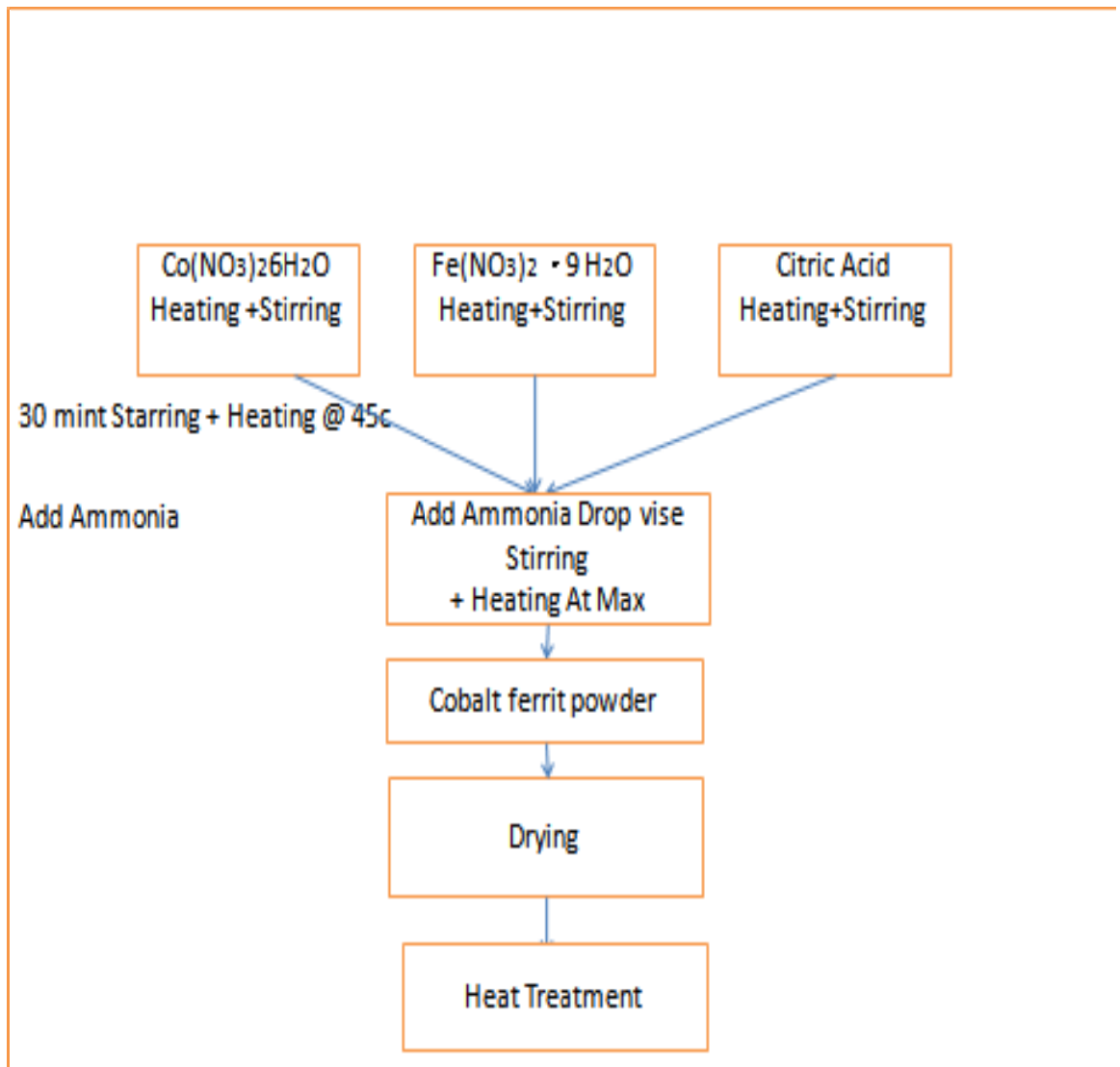


Figure 3.1 schematic of the Sol-gel process

3.3 Synthesis of cobalt ferrite nanoparticles by co-precipitation method

Co-precipitation method is very important method for the synthesis of the nanoparticles. The main advantage of this method is the product obtain is very pure because of washing step in the process. This is also a wet chemical method like sol-gel method. The lab equipment used is listed below.

- Glass jars
- Starring machines

- Magnetic stirrers
- pH meter
- Electric oven
- Mortar and pestle
- Hydraulic press
- Tube furnace

The chemicals used for the synthesis of cobalt ferrite (CoFe_2O_4) are listed below.

- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.1 M
- $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$.2 M
- NaOH (precipitating agent) 1.5M, 2M,3M
- Deionized water

Three different samples are made by the co-precipitation methods. The main difference is the molarity of the precipitating agent. Firstly cobalt nitrate six hydrated ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 5.82 gm are added to 200 ml deionized water to make a .1M solution. Then iron nitrate nine hydrated ($\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$) 16.16 gm is dissolved into 200 ml deionized water to make a .2M solution. The precipitation agent NaOH 12gm is added in 200 ml to form 1.5M solution. Three different solutions are the put on the magnetic stirring machines separately. Stirring and heating at 50°C is continued for half an hour. After a good mixing of each the solutions of metal salts are mixed together in a single jar. Then the precipitating agent is added drop wise in the solution of metal salts. Very fine nanoparticles can be obtained by fine control of pH [57]. Now stop heating and continue stirring for 15 mints. After 15 mints stop stirring and let the precipitate to settle down to the bottom of the glass jar. After 3 hours of the settlement of the precipitate the remaining solution is removed. The washing of the precipitate is repeated 5 times. The purpose of washing is to remove the impurities from the precipitates. After washing 5 times the precipitates are put into the electric oven. The temperature of the oven is set on 100°C . When the product is completely dried the powder is placed out side the oven. The powder is mixed homogeneously with the help of mortar and pestle. Then the powder is pressed by 4 ton load with the help of hydraulic press. Disk shaped pellets are obtained form this process. The powder and pellets are placed into a tube furnace for further heat

treatment. The product is placed in tube furnace for 4 hours at 900 °C. The whole process can be shown in the diagram below. This process is repeated for 3 times to develop three different types of samples. The main difference is the molarity of the precipitating agent (NaOH). In first sample we use 1.5 M NaOH, in second sample 2M NaOH and in third sample 3M NaOH. All the samples are then characterized. XRD, EDS, and SEM characterization techniques are applied on each of the sample. Then the electrical and dielectric quantities are measured.

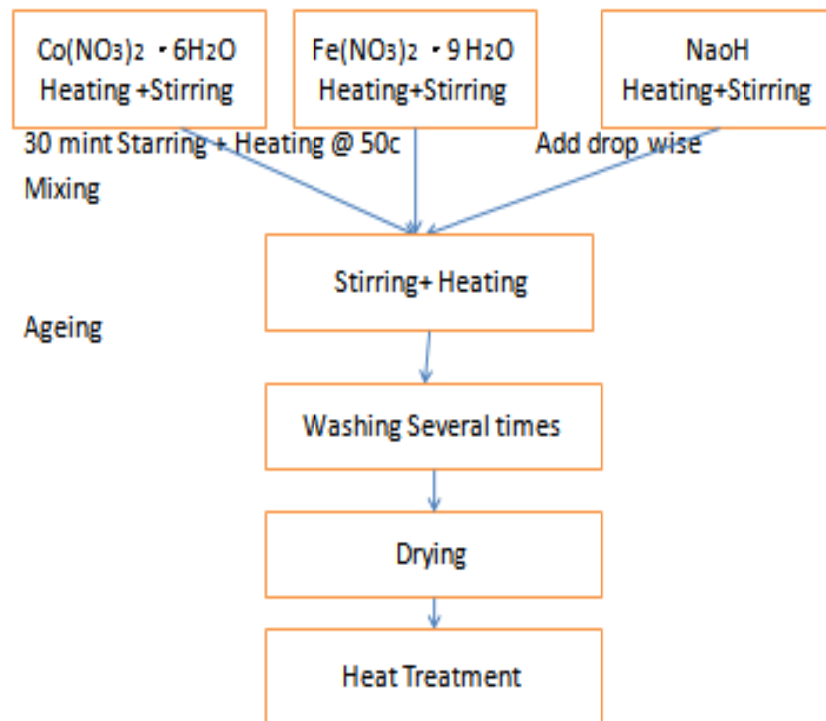


Figure 3.2 Schematic of the chemical co-precipitation process

Chapter 4

Results and Discussions Cobalt Ferrite (CoFe₂O₄)

4.1 Characterization of Cobalt ferrite (CoFe₂O₄)

4.2 Structural Characterization XRD

4.3 Density and Porosity measurements

4.4 Structural characterization by SEM and EDS

4.5 Electrical and Dielectric Properties of Cobalt ferrite (CoFe₂O₄)

4.1 Characterization of cobalt ferrite (CoFe₂O₄)

In this study, the structural and electrical properties of lab synthesis cobalt ferrite are discussed. The cobalt ferrite samples are prepared by both of the techniques.

- (a) Sol-gel
- (b) Chemical co-precipitation

Four types of samples are fabricated by using these two techniques. The samples are in powder form for the study of structural properties and in pellets form to study the electrical properties. One sample made by the sol-gel process and three by the chemical co-precipitation process depending on the molarity of the precipitating agent.

The pellets are formed in a steel die with a hydraulic press. Then the pellets are sintered at 900 °C for four hours. The rate of heating is 12 °C/min and then it stay for 4 hours at 900 °C. The samples are furnace cooled. The cooling rate is 5 °C/min. The effect of different synthesis techniques on the structural, electrical and dielectric properties of cobalt ferrite are discussed below.

4.2 Structural characterization by XRD

The cobalt ferrite powder is synthesized by different methods. One sample is prepared by the sol-gel method and the other three are synthesized by co-precipitation technique. The three sample prepared by co-precipitation method are different to each other due to the concentration of the precipitant agent is different these samples. The samples are then heat treated at 900 °C. The XRD patterns of the four different samples of the cobalt ferrites are shown in the figure 4.1, 4.2, 4.3 and 4.4. The XRD patterns show that all the samples have the peaks indicating the spinel structure.

Figure 4.1 shows the diffraction patterns of the sample S1 prepared by the sol-gel method. The presences of the reflection planes conforms the spinel structure of the sample S1. The reflection planes which are observed in the XRD patterns consist of peaks observed on the reflection of planes (111), (220), (311), (222), (400), (422), (511) and (440). The XRD patterns are matched 80% with the card number (ICCD PDF: 00-022-1086). The peaks obtained are sharper which indicates that the material formed is crystalline. The lattice parameter (a) calculated for this sample is

8.3919Å which is very close to the actual value of bulk cobalt ferrite. The average crystallite size can be calculated by using Scherrer formula [58]. Scherrer formula can be written as.

$$D = 0.9 \lambda / \beta \cos\theta$$

Where,

D is the crystallite size; β is the width of the diffraction line.

Scherrer formula is applied on the most intense peak (311) by using its full width at half maximum of the peak (FWHM). The crystallite size calculated for the sample S1 is 53.5 nm.

Figure 4.2 shows the XRD patterns obtained for the sample S2. This sample is prepared by the Co-precipitation method by using 1.5M NaOH. After that it is sintered at 900⁰C. The peaks observed for this sample on the reflection of planes are (111), (220), (311), (222), (400), (422), (511) and (440). This shows the required phase is formed. The XRD patterns matches with the spinel structure of cobalt ferrite. The XRD patterns obtained are matches 72% with card number (ICCD PDF: 00-003-0864). The lattice parameter (a) for this sample is 8.377 Å. The average crystallite size for this sample is calculated by using the Scherrer formula on the most intense peak (311). The average crystallite size obtained for this sample is 21.5 nm.

Figure 4.3 shows the XRD patterns obtained for sample S3. Sample S3 is synthesis by the co-precipitation method by using 2M NaOH. The final product is then sintered at 900⁰C. The peaks obtained at the reflection planes are (111), (220), (311), (222), (400), (422), (511) and (440). The peak shows that the spinel structure of cobalt ferrite is obtained. The XRD patterns 88% matches with the card number (ICCD PDF: 00-022-1086). The lattice parameter measured for S3 is 8.3919Å. The average crystallite size measured against the most intense peak (311) is 35.5 nm.

Figure 4.4 shows the XRD patterns of sample S4. This sample is synthesized by co-precipitation method by using 3M NaOH. The powder is also sintered at 900⁰C. The peaks obtained at the reflection planes are (111), (220), (311), (222), (400), (422), (511) and (440). This proves the formation of spinel cobalt ferrite structure. XRD

patterns 88% matches with card number (ICCD PDF: 00-022-1086). The average crystallite size measured by Scherrer formula is 35.5 nm

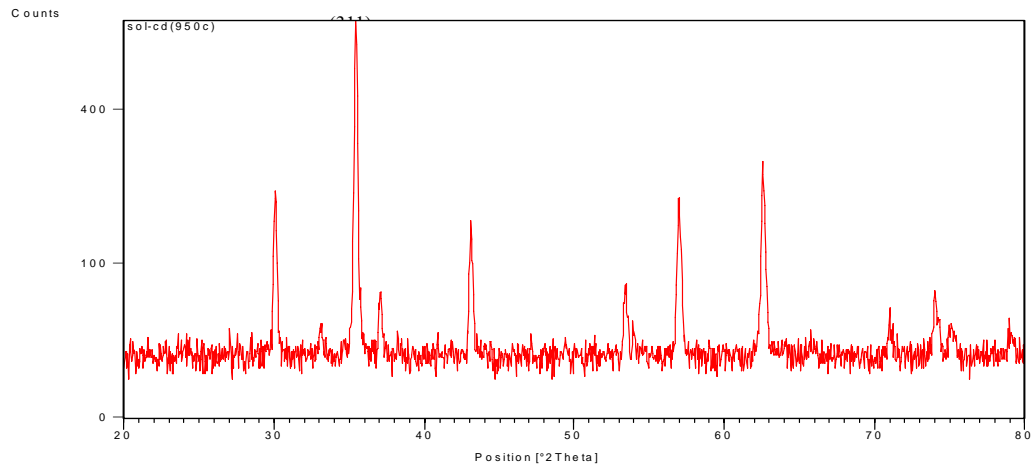


Figure 4.1 XRD patterns of the sample S1 prepared by the sol-gel method

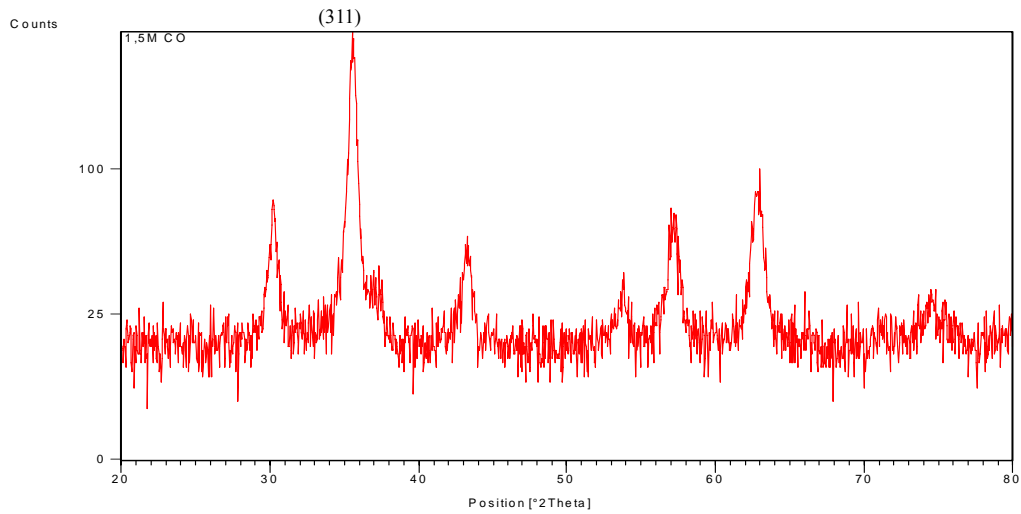


Figure 4.2 XRD patterns of the sample S2 prepared by the chemical co-precipitation method

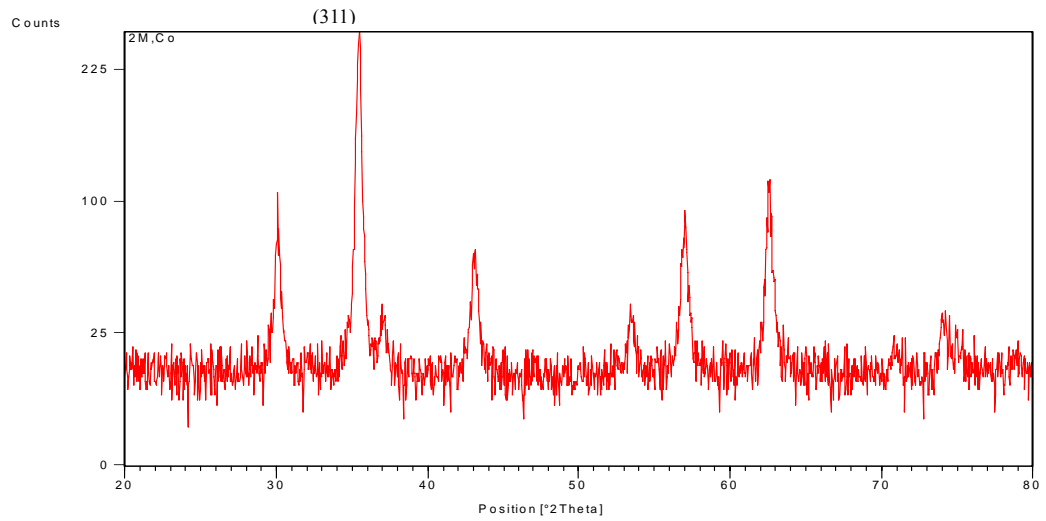


Figure 4.3 XRD patterns of the sample S3 prepared by the chemical co-precipitation method

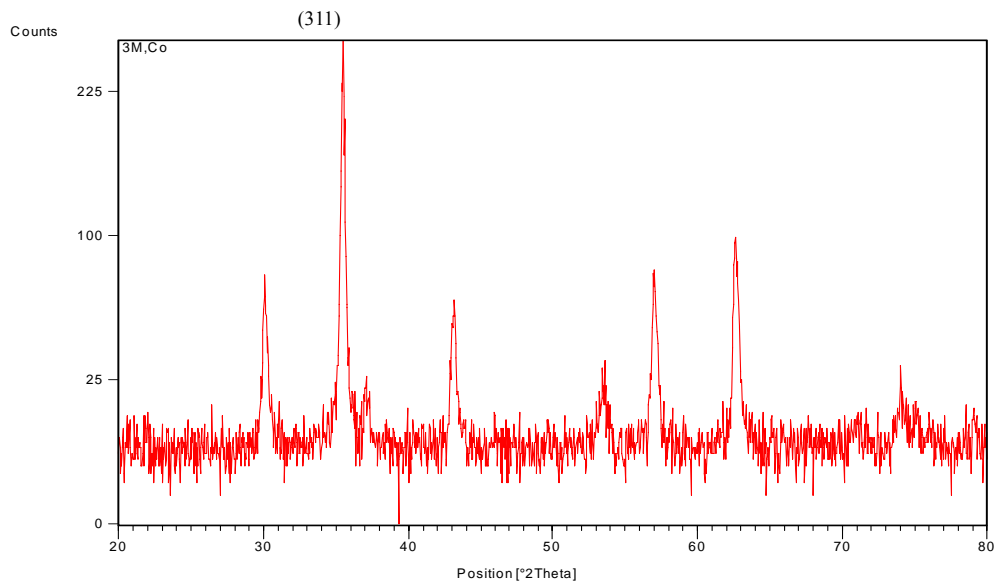


Figure 4.4 XRD patterns of the sample S4 prepared by the chemical co-precipitation method

Average crystallite size in nanometer range is mentioned against each synthesis process. Some of the results from XRD patterns are summarized in the table below.

Table 4.1 Results from XRD technique

<i>Synthesis process</i>	a(Å)	b(Å)	c(Å)	No. of Unit Cells	Average Crystallite Size (nm)
Sol-Gel	8.3919	8.3919	8.3919	8	53.5
Co-precipitation 1.5M	8.377	8.377	8.377	8	21.5
Co-precipitation 2M	8.3919	8.3919	8.3919	8	35.5
Co-precipitation 3M	8.3919	8.3919	8.3919	8	35.5

4.3 Density and porosity measurements

The density of the sample can be calculated by measuring the mass, area, and volume of the sample. The four samples are sintered at 900°C. The formula for the calculation of density is given by the equation.

Where m is the mass of the pellet, h is the thickness and r is the area of the pellet.

The Porosity can also be measured by using the relation given below [59].

$$Porosity (\%) = \left(1 - \frac{D}{D_0}\right) * 100$$

Where D is the calculated density and D_0 is the density calculated by XRD.

The data about the calculated density, theoretical density and the porosity is expressed in the table below.

Table 4.2 Density and porosity measurement.

Synthesis process	Sintering temp °C	D(gm/cm ³)	D_0 (gm/cm ³)	Porosity (%)
Sol-Gel	900	2.37	5.3	55.3
Co-precipitation 1.5M	900	2.27	5.3	57.18
Co-precipitation 2M	900	2.38	5.3	54.96
Co-precipitation 3M	900	2.72	5.3	48.54

4.4 Structural characterization by SEM and EDS

4.4.1 SEM and EDS results for sample S1

The images from the SEM show that the material formed from the sol-gel technique is ultra small. The particle size obtained is of the nanometer range. The average particle size obtained from the SEM results of sample S1 is 64.3 nm. This value is close to the average crystallite size obtained from XRD which is 53.5 nm. In practice SEM particle size always found greater than the XRD crystallite size. EDS patterns show the compositional purity as shown in figure 4.6.

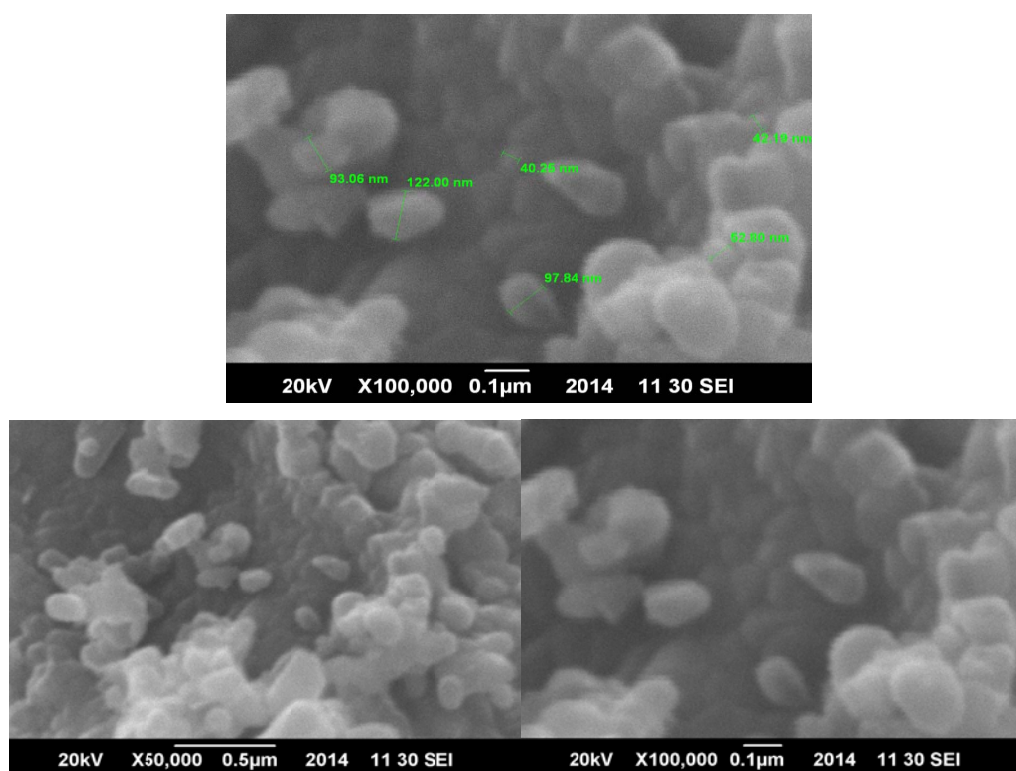


Figure 4.5 SEM images of the sample S1

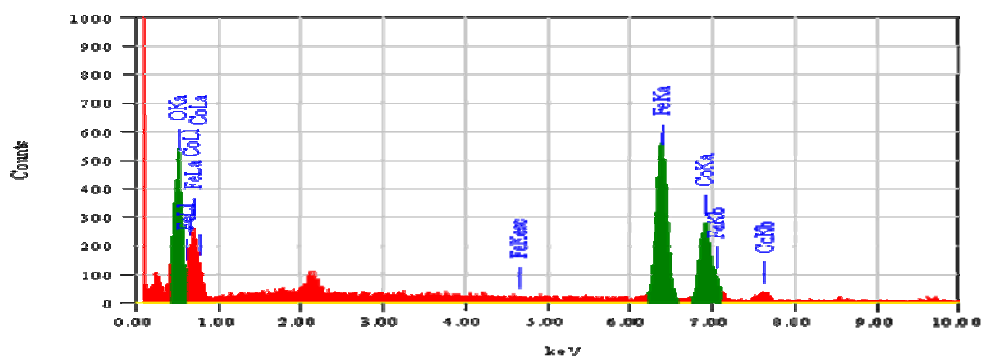


Figure 4.6 EDS pattern of sample S1

4.4.2 SEM and EDS results for sample S2

Figure 4.7 shows that the particle size of the material is in the nanometer range. Agglomeration of the particles can also be observed from the SEM images. Average particle size calculated from SEM images of sample S2 is 32.1 nanometer. This value is also greater than the value of average crystallite size measured by the XRD. EDS results also confirmed the presence of Co, Fe and O in the sample. This also shows the compositional purity.

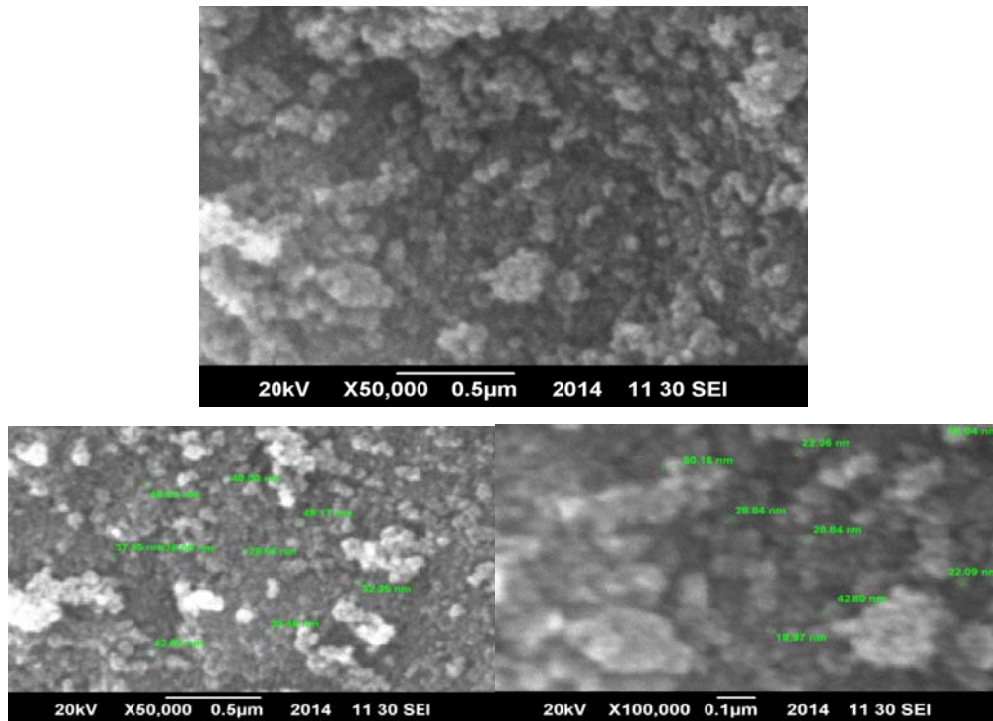


Figure 4.7 SEM images of the sample S2

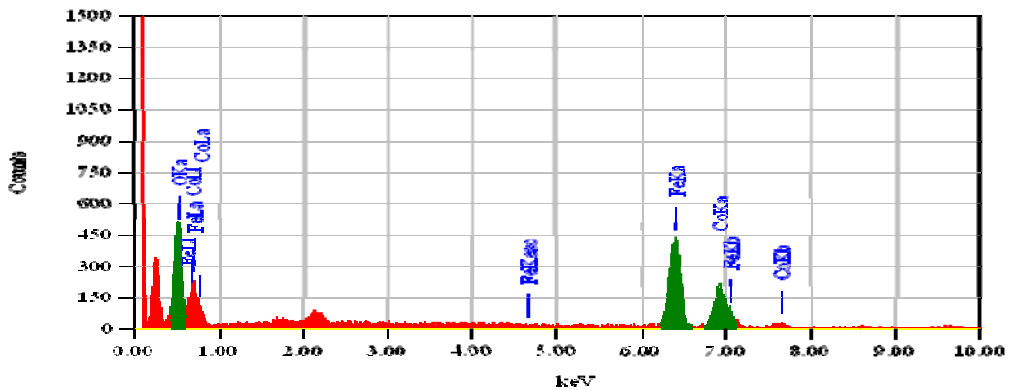


Figure 4.8 EDS pattern of sample S2

4.4.3 SEM and EDS results for sample S3

It can be easily seen from the figure 4.9 that the particle size obtained is in the Nano meter range. The EDS patrons verify the compositional purity of the sample when tested at different points. EDS result shows there are no any impurity present in the sample.

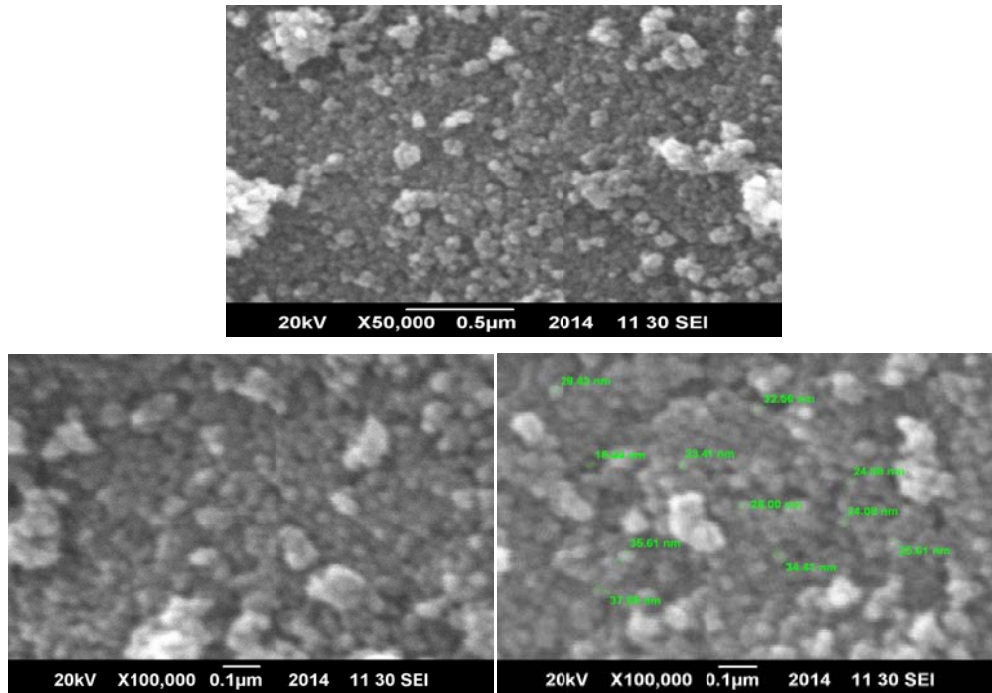


Figure 4.9 SEM images of the sample S3

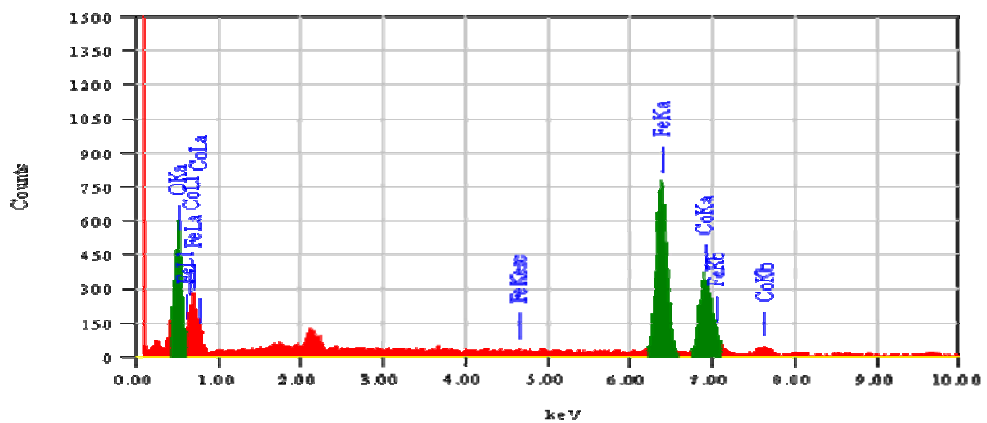


Figure 4.10 EDS pattern of sample S3

4.4.4 SEM and EDS results for sample S4

SEM results shows that the particle size in the nanometer range as shown in the figure 4.11. EDS result also shows the compositional purity of the samples.

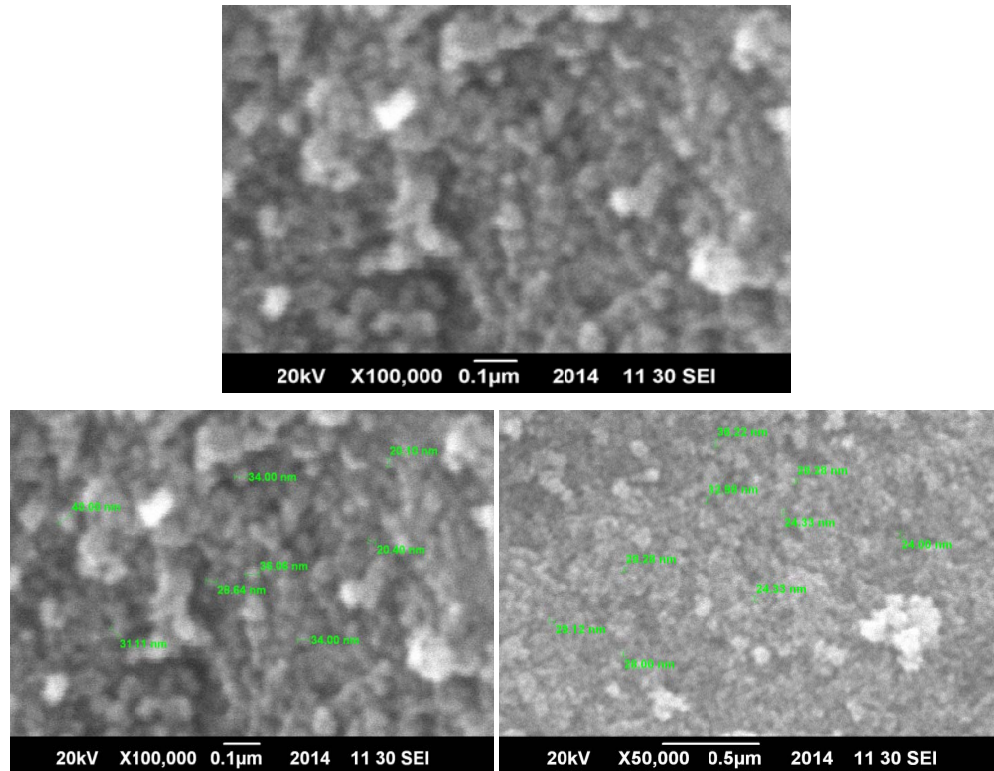


Figure 4.11 SEM images of the sample S4

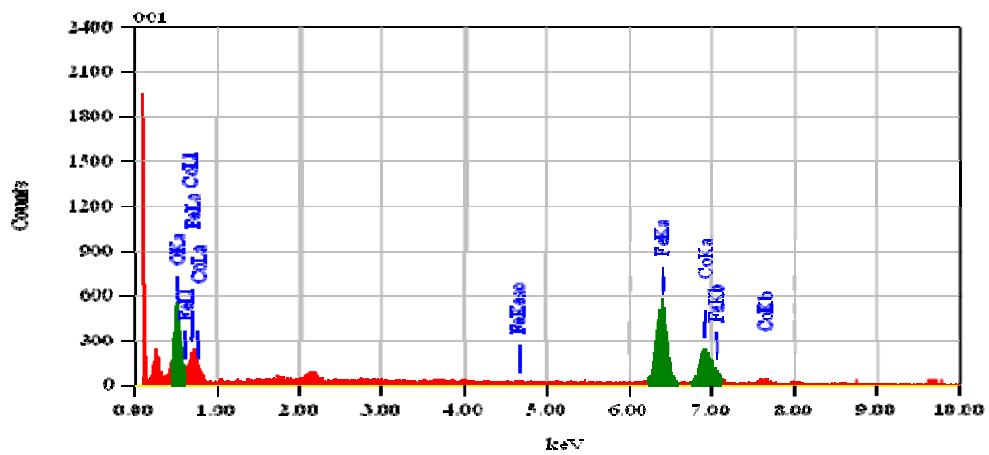


Figure 4.12 EDS pattern of sample S4

4.5 Electrical and Dielectric Properties of Cobalt ferrite (CoFe_2O_4)

Different electrical and dielectric properties are measured against the each sample of prepared cobalt ferrite (CoFe_2O_4).we named the samples as following.

- S1 cobalt ferrite (CoFe_2O_4) prepared by the sol-gel technique
- S2 cobalt ferrite (CoFe_2O_4) prepared by the co-precipitation (1.5 M NaOH)
- S3 cobalt ferrite (CoFe_2O_4) prepared by the co-precipitation (2 M NaOH)
- S4 cobalt ferrite (CoFe_2O_4) prepared by the co-precipitation (3 M NaOH)

Values of dielectric constant are measured against each of the sample in the frequency range 100 Hz to 5MHz. The whole of the data of four samples is compiled in the graph (4.1). Each of the samples has the maximum value of dielectric constant at 100Hz. The graph shows that the maximum dielectric constant value is posses by the S4 at 100Hz frequency. On increasing the value of the frequency towards the higher values the dielectric constant decreases. In the beginning the fall is very rapid but at the end it tends to be flat. In sample number S4 the fall in the value of dielectric constant is very rapid as compared to the other samples. The value of ϵ' fall very slowly with increase in frequency range in samples S1 and S2. S3 have the intermediate rate of fall in the value of ϵ' with increasing frequency range. The dielectric behavior can be explained by the Koop's dielectric theory [60] and Maxwell-Wagner model [61]. Koop explain the variation of dielectric constant in the sense that the conductive grains are separated by the less conductive grain boundaries. Maxwell-Wagner stated that the moving charges are stopped at the boundaries and interfaces that's why the polarization increases. In our case as we have seen the as the frequency is low the dielectric constant has the higher value. When the frequency increases the boundaries show low resistance so the value of dielectric constant falls. Our case obeys both the theories. Dielectric loss is also measured against each sample in the range of frequencies from 100Hz to 5 MHz. experimental data is compiled in the graph shown in the figure 4.14 Dielectric losses has the maximum value at

the initial frequency ranges. Figure 4.13 and 4.14 show that the dielectric losses are maximum when the dielectric constant is maximum. As the resistance is very high at the low frequencies so the dielectric loss is high at that frequencies range. Sample number S4 have a rapid fall in the value of dielectric loss as compared to the other samples. Samples S1 and S2 have the flatter curves as compared to the S3 and S4.

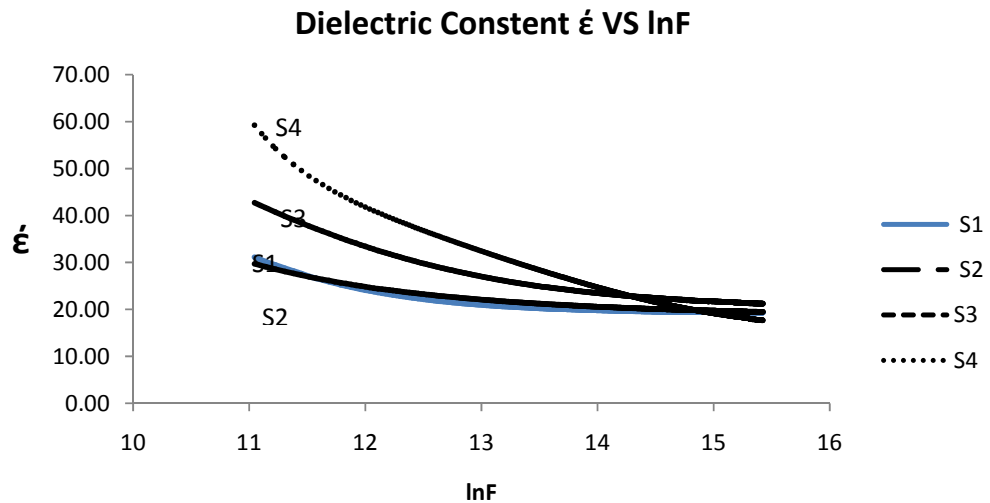


Figure 4.13 graph between dielectric constant ϵ' VS $\ln F$

Figure 4.15 shows the graph between ac conductivity variations with the frequency. The conductivity increases with increase of frequency in every sample. Conductivity increases in the sample S4 is rapid as compared to the samples S2 and S3. This shows that the molarity of the NaOH increases the conductivity.

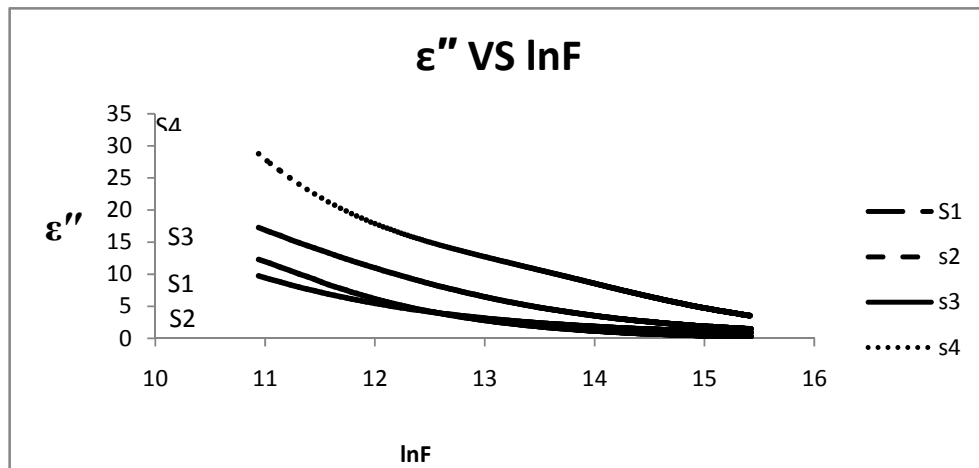


Figure 4.14 graph between dielectric loss ϵ'' VS $\ln F$

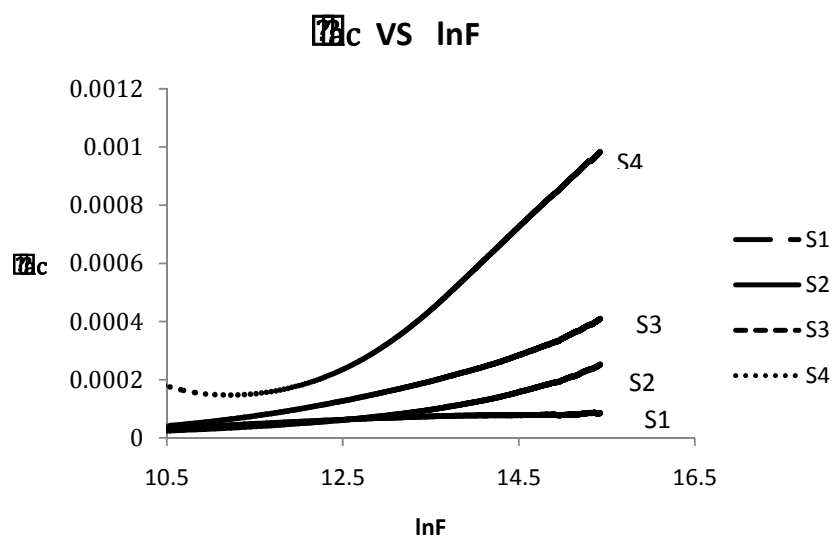


Figure 4.15 Graph between ac conductivity σ_{ac} VS $\ln F$

Table 4.3 shows the value of resistivity against each of the sample. Sample S1 has the largest value of resistivity and sample S2, S3, and S4 shows the gradual increase in the value of resistivity. So resistivity increases with the increase in value of molarity of NaOH.

Table 4.3 Values of resistivity measured of each sample by dc source meter

Synthesis process	Resistivity (Ω cm)	Conductivity(Ω cm) ⁻¹
Sol-Gel	1.15E+06	8.72E-07
Co-precipitation 1.5M	1.93E+04	5.17E-05
Co-precipitation 2M	4.11E+04	2.44E-05
Co-precipitation 3M	1.39E+05	7.17E-06

Table 4.4 Values of ϵ' , ϵ'' and σ_{ac} at different frequencies

<i>Synthesis process</i>	ϵ' <i>1M Hz</i>	ϵ' <i>5M Hz</i>	ϵ'' <i>1MHz</i>	ϵ'' <i>5M Hz</i>	σ_{ac} $(\Omega \text{ cm})^{-1}$ <i>1 M Hz</i>	σ_{ac} $(\Omega \text{ cm})^{-1}$ <i>5 MHz</i>
Sol-Gel	19.9	1.93E+01	1.38	0.302	7.68E-05	8.39E-05
Co-precipitation 1.5M	20.8	1.95E+01	2.03	0.906	1.13E-04	2.52E-04
Co-precipitation 2M	24.0	2.12E+01	3.96	1.48	2.21E-04	4.10E-04
Co-precipitation 3M	26.0	1.77E+01	9.49	3.54	5.28E-04	9.84E-04

Table 4.3 shows that the value of dielectric constant ϵ' at low frequency is lowest for the sample prepared by the sol-gel process. The samples prepared by the chemical co-precipitation process shows that the value of dielectric constant increases on increasing the molarity of the precipitant agent. At higher frequencies the value of dielectric constant is lowest for the sample prepared by the chemical co-precipitation method with 3M NaOH. Highest value of dielectric constant ϵ' at 5 MHz is of the sample prepared by the chemical co-precipitation method with 2M NaOH. Dielectric loss ϵ'' shows the same behavior for low and high frequencies. Sample S1 has the lowest value of dielectric loss ϵ'' . Table shows that on increasing the molarity of the NaOH the dielectric loss increases. It is maximum for sample S4. AC conductivity σ_{ac} at low and high values of the frequencies also shows the same behavior. AC conductivity σ_{ac} has the highest value for the sample S1. In sample S2.S3 and S4 ac conductivity decrease with increasing the molarity of the NaOH.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

5.2 Future Work

5.1 Conclusions

1. Synthesis of cobalt ferrite nanoparticles is successfully achieved by the both sol-gel and chemical co-precipitation processes by using the nitrates of cobalt and Iron, chelating agent citric acid for sol-gel and sodium hydroxide (NaOH) precipitating agent for co-precipitation method. Sample S1 is prepared by the sol-gel method and samples S2, S3, S4 were prepared by co-precipitation method. Molarity of NaOH in S2, S3, and S4 was 1.5M, 2M and 3M respectively .The samples are then sintered for 4 hours at 900⁰C.
2. XRD results confirmed the required phase formation with no extra peaks present. The average crystallite size measured by Scherrer formula for the sample prepared by sol-gel method (S1) is 53.5 nm and average crystallite size measured for samples prepared by the co-precipitation method are 21.5, 35.5 and 35.5 for samples S2, S3, and S4 respectively. It is concluded that crystallite size is larger in sample prepared by sol-gel.
3. SEM images confirmed the nanostructure of the product obtained from both the processes. SEM results also show that the particle size is not uniform for the sample prepared by sol-gel method and uniform for samples prepared by the co-precipitation method. EDS shows the compositional purity of all the samples.
4. Results showed that the porosity decreases with increasing the molarity of precipitating agent in the chemical Co-precipitation method.
5. Value of dielectric constant at 1 MHz is lowest for the sample prepared by the sol-gel method. Dielectric constant has the larger value at 1 MHz for samples prepared by co-precipitation method. The value of dielectric constant also increases with the increase of molarity of the NaOH.
6. Value of dielectric loss is lowest for the sample prepared by the sol-gel method. Dielectric loss increases with the increase in molarity of NaOH in samples prepared by the co-precipitation method. S1 is best candidate for micro-

wave applications due to low value of dielectric loss for the sample prepared by the sol-gel method.

7. AC conductivity values rise rapidly with the increasing the value of frequencies in samples prepared by co-precipitation method. AC conductivity rises very slowly with frequency in case of sample prepared by the sol-gel.
8. DC resistivity has the highest value for sample prepared by sol-gel method. It is also observed that the dc resistivity increases with molarity of NaOH in samples prepared by co-precipitation method. So sample prepared by the sol-gel method is best candidate for the high frequency applications.

5.2 Future Work

Variation of electrical and dielectric properties will be done as a function of temperature. Magnetic properties will also be done at room temperature by using vibrating sample magnetometer. Doping of different impurities will be done to see the variation in the electrical, dielectric and magnetic properties. For the practical application of these materials in the field of micro-electronics thin film formation is necessary. A work will also be done on the thin film formation using Spin coating technique. A comparative study of the properties of nanoparticles and thin film will be done.

References

1. N Lubick "Silver socks have cloudy lining". *Environ SciTechnol* 42 (11): 3910(2008).
2. H. Gleiter, *Prog. Mater. Sci.* 33, 223 (1989).
3. R. W. Siegel, in "Nanomaterials: Synthesis, Properties and Applications," edited by A. S. Edelstein and R. C. Cammarata, IOP Publishing, Philadelphia, p. 201(1998).
4. D. N. Srivastava, N. Perkas, A. Gedanken, and I. Felner, *J. Phys. Chem. B* 106, 1878 (2002).
5. Abraham, SathyaAchia (20). "Researchers Develop Buckyballs to Fight Allergy". Virginia Commonwealth University Communications and Public Relations.
http://www.news.vcu.edu/news/Researchers_Develop_Buckyballs_to_Fight_Allergy.
6. R. M. Bozorth, *Ferromagnetism*. New York: Editorial Board, (1993).
7. W. Callister, *Materials science and engineering an introduction*, Sixth ed. New York: JoHn Wiley & Sons, Inc, (2003).
8. L. Néel, Propriétés magnétiques des ferrites; Férrimagnétisme et antiferromagnétisme, *Annales de Physique (Paris)* 3, 137–198 (1948).
9. Carter, C. Barry; Norton, M. Grant "Ceramic materials: science and engineering" Springer, 2007.
10. N. Spaldin, *Magnetic materials: Fundamentals and device applications*. Cambridge: Cambridge University press, 2003.
11. A. Goldman, *Modern Ferrite Technology*. New York: Van Nostrand Reinhold, 1990.

12. J. Smil, and H.P.J.Wijn, Ferrites, Philips Technical Library Netherlands (1959).
13. A. Kalendová, D. Veselý, J. Brodinová, "Anticorrosive spinel-type pigments of the mixed metal oxides compared to metal polyphosphates", *Anti-Corrosion Methods and Materials*, Vol. 51(2004). Iss: 1, pp.6 – 17.
14. Y.Ceden o-MatteiO.Perales-Perez, *microelectronics Journal* 40 (2009) 673–676.
15. F. Zhang, S. Kantake, Y. Kitamoto, M. Abe, *IEEE Trans. Magn.* 35 (1999) 2751– 2753.
16. I.H. Gul, A. Maqsood, M. Naeem, M. NaeemAshiq, *Journal of Alloys and Compounds* 507 (2010) 201–206.
17. L. D. Tung, V. Kolesnichenko, D. Caruntu, N. H. Chou, C. J. O'Connor, and L. Spinu, "Magnetic properties of ultrafine cobalt ferrite particles," *Journal of Applied Physics*, vol. 93., pp. 7486-7488,(2003).
18. N. Feltin and M. P. Pileni, "New technique for synthesizing iron ferrite magnetic nanosized particles," *Langmuir*, vol. 13, pp. 3927-3933, (1997).
19. V. Blaskov, V. Petkov, V. Rusanov, L. M. Martinez, B. Martinez, J. S. Munoz, and M. Mikhov, "Magnetic properties of nanophase CoFe₂O₄ particles," *Journal of Magnetism and Magnetic Materials*, vol. 162, pp. 331-337, (1996).
20. S. Li, L. Liu, V. T. John, C. J. O'Connor, and V. G. Harris, "Cobalt-ferrite nanoparticles: Correlations between synthesis procedures, structural characteristics, and magnetic properties," presented at 8th Joint Magnetism and Magnetic Materials -International Magnetic Conference- (MMM-Intermag), Jan 7-11 (2001), San Antonio, TX, (2001).
21. N. Moumen, P. Veillet, and M. P. Pileni, "Controlled preparation of nanosize cobalt ferrite magnetic particles," *Journal of Magnetism and Magnetic Materials Proceedings of the 7th International Conference on Magnetic Fluids*, Jan 7-14 (1995), vol. 149, pp. 67-71, (1995).

22. V. Pillai and D. O. Shah, "Synthesis of high-coercivity cobalt ferrite particles using water-in-oil microemulsions," *Journal of Magnetism and Magnetic Materials*, vol. 163, pp. 243-248, (1996).
23. P.A.Shaikh,R.C.Kamble,A.V.Rao,Y.D.Kolekar "Studies on structural and electrical properties of $\text{Co}_{1-x}\text{Ni}_x\text{Fe}_{1.9}\text{Mn}_{0.1}\text{O}_4$ ferrite" ,*Journal of Alloys and Compounds*,482,pp276-282,(2009).
24. A.Verma, T.C.Goel, R.C.Mendiratta, M.I.Alam, "Dielectric properties of NiZn ferrites prepared by the citrate precursor method", pp156-161, (1999).
25. M.Kaiser, S.S.Ata-Allah," Mossbauer effect and dielectric behavior of $\text{Ni}_x\text{Cu}_{0.8-x}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ Compound", *Materials Research Bulletin*, 44, pp1249-1255, (2009).
26. R. W. Siegel, in "Physics of new materials," edited by F. E. Fujita, Springer-Verlag, Berlin, Germany, (1994).
27. S. E. Pratsinis and T. T. Kodas, in "Aerosol measurement," edited by K. Willeke and P. A. Baron, Van Nostrand Reinhold, New York, (1993).
28. T. T. Kodas and M. J. H. Smith, "Aerosol processing of materials," Wiley-VCH, New York, (1999).
29. W. J. Dawson, *Am. Ceram. Soc. Bull.* 67, 1673 (1988).
30. S. Somiya and R. Roy, *Bull. Mater. Sci.* 23, 453 (2000).
31. O'Donoghue, M. *A guide to Man-made Gemstones*. Great Britain: Van Nostrand Reinhold Company. pp. 40–44(1983).
32. W. J. Dawson, *Am. Ceram. Soc. Bull.* 67, 1673 (1988).
33. P. Ravindranathan and K. C. Patil, *Am. Ceram. Soc. Bull.* 66, 688 (1987).
34. D. Majumdar, H. D. Glicksman, and T. T. Kodas, *Powder Technol.* 110, 76 (2001).
35. T. T. Kodas and M. J. H. Smith, "Aerosol processing of materials," Wiley- VCH, New York, (1999).
36. K. Shantha, G. N. Subbanna, and K. B. R. Varma, *J. Solid State Chem.* 142, 41 (1999).
37. Livage, J. "Sol-Gel Synthesis of Heterogenous Catalysts from Aqueous Solutions". *Catalysis Today*. 41. 3-19(1998).

38. Ju, X. S., Huang, P., Xu, N. P., and Shi, J. "Influences of Sol and Phase Stability on the Structure and Performance of Mesoporous Zirconia Membranes". *Journal of Membrane Science*. 166. 41-50(2000).
39. Choi, D. G., and Yang, S. M. "Effect of Two-Step Sol-Gel Reaction on the Mesoporous Silica Structure". *Journal of Colloid and Interface Science*. 261. 127-132(2003).
40. [www.asso.dem.pagesperso-orange](http://www.asso.dem.pagesperso-orange.fr).
41. MacKenzie JD. Sol-gel research – achievements since 1981 and prospects for the Future. *J. Sol-Gel Sci. Techn.*26:23–27(2003).
42. Lambert, C. K., and Gonzalez, R. D. "The Effect of pH and Metal Loading on the Properties of Sol-Gel Rh/SiO₂". *Journal of Solid State Chemistry*. 158. 154-161(2001).
43. Gonzalez, R. D., Lopez, T., and Gomez, R. "Sol-Gel Preparation of Supported Metal Catalysts". *Catalysis Today*. 35. 293-317(1997).
44. J. Park, V. Privman, E. Matijevic, *J. Phys. Chem. B*, 105 (2001) 11630.
45. <http://en.wikipedia.org/wiki/File:Co-precipitation.png>
46. R Massart, E. Dubois, V Cabuil, E Hasmonay, *J. Magn. Magn. Mater.* 149 (1995) 1
47. Q. Li, T. Sasaki, and N. Koshizaki, *Appl. Phys. A* 69, 115 (1999).
48. A. Guinier, *X ray Diffraction*, San Francisco, CA , (1963).
49. M. Watt, *The Principles and Practice of Electron Microscopy*, 2nd Edition, Cambridge University Press, Cambridge (1997)
50. C.T. Schamp, W.A. lesser, *Ultramicroscopy*, 103 (2005) 165
51. ApamaRoy ,V. Srinivas, S. Ram, I. A. De Toro, *J. Appl. Phys.* 100 (2006)
52. D. C. a. N. Dube, R, J., *Appl. Phys.*, (1973).
53. F. C. Brown, "The physics of solids," (1967).
54. K. a. M. Kaniyoshi, T. J., *Chem .Phys.*,(1954).
55. J.L Dormann, D Fiorani, *J. Magn. Magn. Mater.* 140-144 (1995) 415.

56. MacKenzie JD. Sol-gel research – achievements since 1981 and prospects for the Future. *J. Sol-Gel Sci. Techn.* 2003;26:23–27
57. J. Park, V. Privman, E. Matijevic, *J. Phys. Chem. B*, 105 (2001) 11630.
58. B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Reading, MA, , p. 102(1978).
59. C. Koop's, "On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audio frequencies," *Physical Review*, vol. 83, pp. 121-124, (1951).
60. P. Fulay, "Electronic, Magnetic and Optical Materials," book, (2010)

References

1. N Lubick, Environ Sci Technol. 11(2008)42.
2. H. Gleiter, Prog, Mater. Sci. 33 (1989) 223.
3. R. W. Siegel, A. S. Edelstein and R. C. Cammarata, IOP Publishing, Philadelphia. 201(1998)455.
4. D. N. Srivastava, N. Perkas, A. Gedanken, and I. Felner, J. Phys. Chem. 106 (2002) 1878.
5. http://www.news.vcu.edu/news/Researchers_Develop_Buckyballs_to_Fight_Allergy.
6. R. M. Bozorth, Ferromagnetism. New York: Editorial Board, (1993).
7. W. Callister, Materials science and engineering an introduction, Sixth ed. New York: John Wiley & Sons, Inc, (2003).
8. L. Néel, Propriétés magnétiques des ferrites; Ferrimagnétisme et antiferromagnétisme, Annales de Physique (Paris). 3 (1948) 198.
9. Carter, C. Barry; Norton, M. Grant "Ceramic materials: science and engineering" Springer, (2007).
10. N. Spaldin, Magnetic materials: Fundamentals and device applications. Cambridge: Cambridge University press, (2003).
11. A. Goldman, Modern Ferrite Technology. New York: Van Nostrand Reinhold, (1990).
12. J. Smil, and H.P.J. Wijn, Ferrites, Philips Technical Library Netherlands (1959).
13. A. Kalendová, D. Veselý, J. Brodinová, Anti-Corrosion Methods and Materials, . 51(2004) 6 – 17.
14. Y. Ceden o-Mattei O. Perales-Perez, microelectronics Journal 40 (2009) 673–676.
15. F. Zhang, S. Kantake, Y. Kitamoto, M. Abe, IEEE Trans. Magn. 35 (1999) 2751– 2753.

16. I.H. Gul, A. Maqsood, M. Naeem, M. NaeemAshiq, *Journal of Alloys and Compounds*. 507 (2010) 201–206.
17. L. D. Tung, V. Kolesnichenko, D. Caruntu, N. H. Chou, C. J. O'Connor, and L. Spinu, *Journal of Applied Physics*. 93(2003) 7486-7488.
18. N. Feltin and M. P. Pileni, *Langmuir*. 13 (1997) 3927-3933.
19. V. Blaskov, V. Petkov, V. Rusanov, L. M. Martinez, B. Martinez, J. S. Munoz, and M. Mikhov, *Journal of Magnetism and Magnetic Materials*. 162 (1996) 331-337.
20. S. Li, L. Liu, V. T. John, C. J. O'Connor, and V. G. Harris, *MMM-Intermag*. 7(2001) 11.
21. N. Moumen, P. Veillet, and M. P. Pileni, *Journal of Magnetism and Magnetic Materials*. 149 (1995) 67-71.
22. V. Pillai and D. O. Shah, *Journal of Magnetism and Magnetic Materials*. 163 (1996) 243-248.
23. P.A.Shaikh, R.C.Kamble, A.V.Rao, Y.D.Kolekar, *Journal of Alloys and Compounds* .482(2009) 276-282.
24. A.Verma, T.C.Goel, R.C.Mendiratta, M.I.Alam, *Mater Sci Eng*. 60(1999)161.
25. M.Kaiser, S.S.Ata-Allah, *Materials Research Bulletin*. 44(2009) 1249.
26. R. W. Siegel, in “Physics of new materials,” edited by F. E. Fujita, Springer-Verlag, Berlin, Germany, (1994).
27. S. E. Pratsinis and T. T. Kostas, in “Aerosol measurement,” edited by K. Willeke and P. A. Baron, Van Nostrand Reinhold, New York, (1993).
28. T. T. Kostas and M. J. H. Smith, “Aerosol processing of materials,” Wiley-VCH, New York, (1999).
29. W. J. Dawson, *Am. Ceram. Soc. Bull*. 67 (1988) 1673.
30. S. Somiya and R. Roy, *Bull. Mater. Sci*. 23 (2000) 453.

31. O'Donoghue, M. *A guide to Man-made Gemstones*. Great Britain: Van Nostrand Reinhold Company. (1983) 40–44.
32. W. J. Dawson, *Am. Ceram. Soc. Bull.* 67 (1988) 1673.
33. P. Ravindranathan and K. C. Patil, *Am. Ceram. Soc. Bull.* 66 (1987) 688.
34. D. Majumdar, H. D. Glicksman, and T. T. Kodas, *Powder Technol.* 110 (2001) 76.
35. T. T. Kodas and M. J. H. Smith, “Aerosol processing of materials,” Wiley- VCH, New York, (1999).
36. K. Shantha, G. N. Subbanna, and K. B. R. Varma, *J. Solid State Chem.* 142 (1999) 41.
37. Livage, J. *Catalysis Today.* 41(1998) 19.
38. Ju, X. S., Huang, P., Xu, N. P., and Shi, J, *Journal of Membrane Science.* 166(2000) 49.
39. Choi, D. G., and Yang, S. M, *Journal of Colloid and Interface Science.* 261(2003)129.
40. www.asso.dem.pagesperso-orange.
41. MacKenzie JD. Sol-gel research – achievements since 1981 and prospects for the Future. *J. Sol-Gel Sci. Techn.*26 (2003) 27.
42. Lambert, C. K., and Gonzalez, R. D, *Journal of Solid State Chemistry.* 158 (2001)159.
43. Gonzalez, R. D., Lopez, T., and Gomez, R, *Catalysis Today.* 35(1997) 293.
44. J. Park, V. Privman, E. Matijevic, *J. Phys. Chem. B,* 105 (2001) 11630.
45. <http://en.wikipedia.org/wiki/File:Co-precipitation.png>
46. R Massart, E. Dubois, V Cabuil, E Hasmonay, *J. Magn. Magn. Mater.* 149 (1995) 1
47. Q. Li, T. Sasaki, and N. Koshizaki, *Appl. Phys. A* 69, 115 (1999).
48. A. Guinier, *X ray Diffraction*, San Francisco, CA , (1963).
49. M. Watt, *The Principles and Practice of Electron Microscopy*, 2nd Edition, Cambridge University Press, Cambridge (1997)

50. C.T. Schamp, W.A. lesser, *Ultramicroscopy*, 103 (2005) 165
51. S. Ram, A. Jana, and T. K. Kundu *J. Appl. Phys.*, **102** (2007) **54107**.
52. D. C. Dube and R. Natarajan, *J. Appl. Phys.* **44** (1973)4927.
53. F. C. Brown, "The physics of solids," (1967).
54. K. a. M. Kaniyoshi, T. J., *Chem .Phys.*, (1954).

55. J.L Dormann, D Fiorani, *J. Magn. Magn. Mater.* 140-144 (1995) 415.
56. MacKenzie.JD ,*Sol-Gel Sci. Techn.* 26 (2003) 27.
57. J. Park, V. Privman, E. Matijevic, *J. Phys. Chem.*105 (2001) 11630.
58. B.D. cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Reading, MA. (1978).
59. C. Koop's. 83 (1951) 121-124.
60. P. Fulay, "Electronic, Magnetic and Optical Materials," book, (2010)