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Shri Swami Vivekanand Shikshan Sanstha's

## Vivekanand College (Autonomous) Kolhapur

Department of Physics

M.Sc. II (2018-19)

### Research Project Title

Roll No.	Name of Students	Name of Guide	Title of Project
1501	Aswale Nikhil Mohan	Prof. A.V. Shinde	Deposition of Copper Oxide thin film by Reflux method
1502	Bachate Prajakta Ramchandra	Dr. M. M. Karanjkar	Deposition of MnO <sub>2</sub> Thin Film by SILAR Method
1503	Deshmukh Namita Prataprao	Dr. M. M. Karanjkar	Synthesis and Characterization Zinc Ferrite by Microwave Assisted Method
1504	Ghadage Sachin Subhash	Dr. M. M. Karanjkar	Synthesis and Characterization of ZnO thin film by Successive Ionic Layer of Adsorption and Reaction Method and It's Application
1505	Jadhav Anmol Narendra	Dr. M. M. Karanjkar	Synthesis of ZnO Thin Film By Spray Pyrolysis Technique
1506	Jangid Saroj Nemichand	Dr. M. M. Karanjkar	Synthesis of Fe <sub>2</sub> O <sub>3</sub> thin film by Spray Pyrolysis Technique
1507	Kamble Karan Mukund	Prof. A.V. Shinde	Deposition of MnO <sub>2</sub> thin film by SILAR method
1508	Kjhan Anjum Ibrahim	Prof. A.V. Shinde	Deposition of CdS thin film by Electrodeposition method
1509	Mane Rajlakshmi Sanjay Rao	Dr. M. M. Karanjkar	Preparation of Ni-Zn Ferrite by Microwave Assisted Technique
1510	Mulla Shah Nawaj Barkatali	Dr. M. M. Karanjkar	Preparation of Ni-Zn Ferrite by Microwave Assisted Technique



1511	Nalawade Priyanka Mansing	Prof. S.V. Malgaonkar	Preparation of Ni-Zn Ferrite by Micro wave Assisted Method
1512	Patnkar Shivrasaj Mansing	Prof. S.V. Malgaonkar	Preparation of $Zn_x Cd_{1-x}$ Ferrite by Micro wave Assisted Method
1513	Pathak Onkar Herambraj	Dr. M. M. Karanjkar	Synthesis of $MnO_2$ Thin Film by Electro Deposition Method
1514	Patil Nirmala Vilas	Prof. A.V. Shinde	Deposition of CdS for supercapacitor by CBD
1515	Patil Rasika Chandrakant	Dr. G.J. Navathe	To Prepare $Fe_2O_3$ by Reflux method
1516	Pawar Pooja Guntant	Dr. G.J. Navathe	To deposit $MnO_2$ by electrodeposition method
1517	Phadtare Pooja Sunil	Prof. S.V. Malgaonkar	Preparation of $Zn_{1-x} Cd_x$ Ferrite by Micro wave Assisted Method
1518	Salunkhe Abhishek Chandrashekhar	Dr. G.J. Navathe	To deposit $MnO_2$ thin film by Electrodeposition method
1519	Shirage Pravin Ramchandra	Dr. M. M. Karanjkar	To deposit $Mg_x Cd_{1-x}$ Ferrite by Micro wave Assisted method
1520	Sid Shraddha Arun	Prof. S.V. Malgaonkar	Preparation of Ni-Zn Ferrite by Sintering method
1521	Waghmore Prasadkumar Bhimrao	Prof. A.V. Shinde	To deposit NiO thin film by CBD

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# **PREPARATION OF Ni-Zn FERRITE BY MICROWAVE ASSISTED TECHNIQUE**

A Dissertation Report Submitted to  
**Vivekanand College (Autonomous),  
KOLHAPUR.**

For the Partial Fulfillment of  
Degree of Master of Science  
In  
**PHYSICS**

Under the Faculty of Science

by

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2018-2019



## DECLARATION

I hereby declare that, the project entitled "**Preparation of Ni-Zn Ferrite by Microwave Assisted Technique**" completed and written by me has not previously formed the basis for the award of any Degree or Diploma or other similar title of this or any other University or examining body.

Place: Kolhapur

Date: 29 - 3 - 19



Miss. NALAWADE PRIYANKA MANSING  
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# CERTIFICATE

This is to certify that the project entitled "Preparation of Ni-Ferrite by Microwave Assisted Technique" which is being submitted herewith for the award of the Degree of Master of Science in Physics of Vivekanand College (Autonomous), KOLHAPUR, is the result of the original project work completed by Miss. Nalawade Priyanka Mansing under our supervision and guidance and to the best of our knowledge and belief the work embodied in this project has not formed earlier the basis for the award of any Degree or similar title of this or any other University or examining body.

Place: Kolhapur

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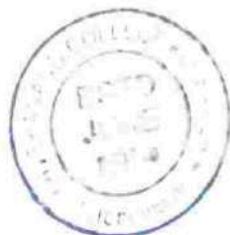
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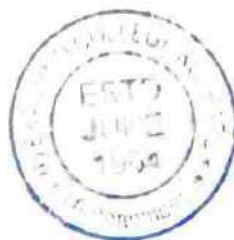
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# INDEX

<b>Sr. No</b>	<b>Content</b>	<b>Page No</b>
1.	Introduction	6-15
2.	Theoretical Background	16-29
3.	Literature Survey	30- 33
4.	Synthesis & Result	34-36
5.	Summary & Conclusion	37-40



# Chapter 1

## Introduction to Ferrites

Sr. No	Content	Page No
1.1	Introduction to Ferrite	6-10
1.2	Magnetism	11-13
1.3	Applications of Ferrite	14
1.4	References	15

### 1.1 Introduction to Ferrites

It is a Ceramic compound consisting of a mixed oxide of iron and one or more other metals which shows ferrimagnetic property. Ferrites are an important class of magnetic materials which have many applications, ranging from radio frequency and microwave frequency. They can be used in Transformers, inductors, antenna rod, memory chip etc. Also, they have found applications in sensor. Ferrites that are used in transformer or electromagnetic cores contain Nickel, zinc or manganese compounds.

Soft ferrites have a low coercivity and are called as soft ferrites. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of switched mode power supply (SMPS) and RF Transformers and inductors. Hard ferrites have a high coercivity. They are magnetically very stable and difficult to demagnetize either by external magnetic field. In terms of magnetic properties, ferrites are often classified as "soft "and" hard", which refers to their low and high coercivity of their magnetism respectively.





## History of Ferrites

Ferrites are the stones that could attract iron or discovered the fourth birth of crest. These stones were found in the district of magnesia in Asia Mina. hence the name magnetite ( $Fe_2O_4$ ). Navigators used magnetite as lodestone to locate magnetic north. The first application of magnetite was as lodestones used by early navigators to locate magnetic north. In 1600, the first scientific study of magnetism names De magnet was published by William Gilbert.

Naturally occurring magnetite is weak hard ferrite. These are permanent magnet. During the 1930's research on soft ferrite continued primarily in Japan and Netherlands. However, it was not until 1945 that J. L. Snoek of the Philips research laboratories in Netherlands succeed in producing a soft ferrite for commercial application.

Ferrites are used predominantly three areas of Electronics

- 1) low level application
- 2) power application
- 3) electromagnetic interference suppression.

In 1952, Hogan constructed the first workable ferrite microwave gyator. The study of microwave ferrite has given impetus to the renewal of interest in solid state Physics.

### • Ferrite

It is a Ceramic compound consisting of a mixed oxide of iron and one or more other metals which shows ferrimagnetic property.

The ferrites are mainly used due to their high resistivity, low Eddy currents, low dielectric losses and high Curie temperature.

### • Types of ferrites

Ferrites based on their structure can be classified into two types

1. Cubic ferrites
2. Hexagonal ferrites



## I. Cubic ferrites

Cubic ferrites are further classified into two groups

- i. Soft ferrites / Spinel ferrites
- ii. Hard ferrites / Garnets

### I. Soft / Spinel ferrites

Soft ferrites are the ones with low coercivity which are used in various applications at high frequencies. These types of ferrites are easy to demagnetize because of their low coercivity. Spinel ferrites or soft ferrites are used as transformer core in television, telecommunication, computer and other industrial electronic system. The structure of soft ferrites is spinel one and that is why they are called spinel ferrites.

Chemical formula for a spinel structure is  $MFe_2O_4$

Where, M is a divalent metal ion (Co, Ni, Mg, Zn, Cd etc.)

#### • Spinel structure

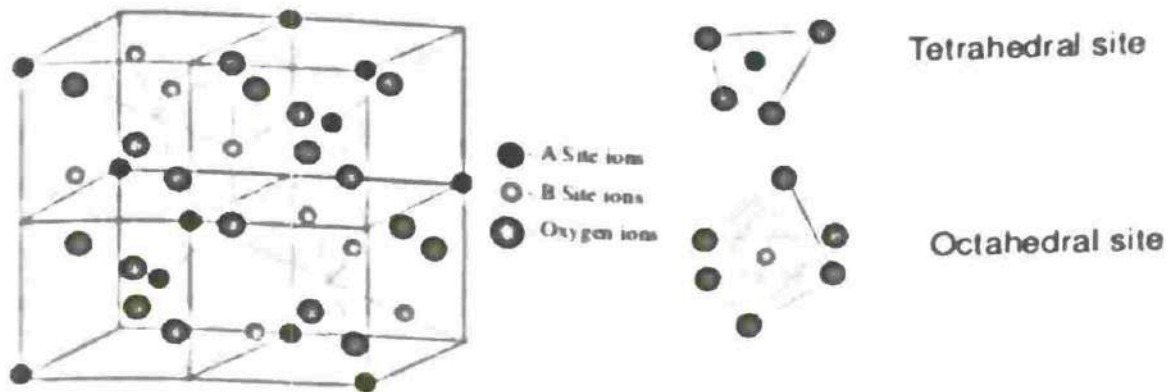
Structural formula spinel structure is  $AB_2O_4$

There is a FCC packing of ions

In any spinel structure there are 56 lattice sites out of which 1/8 tetrahedral and 1/2 octahedral sites are occupied by oxygen that is 32 sites out of 56 sites are occupied by oxygen only and 8 tetrahedral sites and 16 octahedral sites are remaining.



## Crystal structure of Spinel Ferrite



- Spinel structures are of three types

- a) Normal spinel
- b) Inverse spinel
- c) Mixed / Random spinel

- a) **Normal spinel structure**

In normal spinel ferrites eight tetrahedral sites occupied by divalent metal, remaining 16 octahedral sites are occupied by  $\text{Fe}^{3+}$  ions, and all the remaining 32 sites are occupied by oxygen atoms only.

- b) **Inverse spinel structure**

In inverse spinel ferrites 8 tetrahedral sites are occupied by  $\text{Fe}^{3+}$  ions, 8 octahedral sites occupied with remaining  $\text{Fe}^{3+}$  ions, remaining 8 octahedral sites are occupied by divalent metal ions and remaining 32 sites are occupied with oxygen atoms.



## ii. Hard ferrites

Hard ferrites are the ones with high coercivity, and which are difficult to demagnetize.

Chemical formula for hard ferrite is  $\text{Ln}^{3+}\text{Fe}_5\text{O}_{12}$

Where  $\text{Ln}^{3+}$  can be any of the following

$\text{Y}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Dy}^{3+}$  etc.

The coercivity for normal ferrite is in between 100 Oe to 1.5 KOe.

The coercivity for hard ferrite above 1.5 KOe.

## 2. Hexagonal ferrites

These ferrites are Magneto plumbite type ferrites. General formula for hard ferrite is  $\text{MeFe}_{12}\text{O}_{19}$  and this type of material crystallizes in hexagonal structure.

They are classified into M, W, Y, Z and U compounds and all of them have different crystal structure. They are permanent magnetic materials having high coercivity.

Type	Structure	General formula	Examples
Spinel	Cubic	$\text{MFe}_2\text{O}_4$	M = Cd, Co, Mg, Ni, Zn etc.
Garnet	Cubic	$\text{Ln}^{3+}\text{Fe}_5\text{O}_{12}$	$\text{Ln}^{3+} = \text{Y}^{3+}, \text{Sm}^{3+}$ etc.
Magneto plumbite	Hexagonal	$\text{MeFe}_{12}\text{O}_{19}$	Me = Ba, Sr etc.





## 1.2. Magnetism

To research in the field of ferrites one should have to have a basic knowledge of magnetism.

Basically, all materials are magnetic in nature in one way or another. Origin of magnetism in any material arises because of the motion of electrons inside the atoms of a particular material. If each orbit of electron considered as a tiny loop of current when it has certain magnetic moment called orbital magnetic moment. Electron also spins around an axis which produces spin magnetic moment. The resultant magnetic moment of an electron is a vector sum of these two magnetic moments.

In an atom the magnetic moments of core electrons cancel out and magnetic moment of atom is vector sum of magnetic moment of unpaired electrons only.

### Basic terms used in magnetism

- **External magnetic field strength (H): -**

It is the magnetic field which is used to study the magnetic nature of a given material.

Magnetic field is measured in A/m or Oe.

- **Magnetization (M): -**

Net magnetic dipole moment per unit volume he is called magnetization.

Magnetization is a vector quantity and measured in A/m.

- **Susceptibility ( $\chi$ ): -**

Magnetization and external magnetic field intensity are related to each other by susceptibility. Mathematically susceptibility is ratio of magnetization to external magnetic field strength. Susceptibility can be positive or negative. Sign of Susceptibility indicates whether a material is attracted into or repelled out of the magnetic field.

Susceptibility is a dimensionless quantity hence it has no unit.



- **Permeability ( $\mu$ ): -**

Permeability is ability of a material to permit the external magnetic lines of force to go through it. Permeability is also the measure of the ability of a material to support the formation of magnetic field within itself. Mathematically permeability is ratio of induced magnetic field to the external magnetic field strength.

The unit of permeability is henry/m.

- **Types of magnetic materials: -**

Based on magnetic properties of material and the behavior of magnetic moments of the material, substances can be classified into following types.

**1) Diamagnetic material: -**

This type of materials does not contain any unpaired electrons that is why they do not show any magnetic property. When external magnetic field is applied to it, it gets magnetized but in non-cooperative way that is it repels external magnetic field. It shows magnetization is in the exact opposite direction of the external magnetic field. Susceptibility of diamagnetic material is negative and small. After the removal of external magnetic field, it gets demagnetized.

Examples- CuO, Bi etc.

**2) Paramagnetic material: -**

This type of materials has some unpaired electrons and the magnetic moments of all the atoms are oriented randomly and neutralizes each other magnetic moments. This type of materials are also called magnetically dilute system. Paramagnetic materials obey Curie Weiss law. When external magnetic field applied to it, it gets magnetized. it shows magnetization in the direction of external magnetic field. After the removal of external magnetic field, it gets demagnetized.

Susceptibility of a paramagnetic material is positive and greater than 1.



### 3) Ferromagnetic material: -

Each atom of a ferromagnetic materials has certain magnetic moment and there are domains where all the atomic magnets oriented in the same direction. All the domains in a particular ferromagnetic material are randomly oriented and the resultant magnetic field is zero. When external magnetic field is applied to it, all the domains will Orient in the direction of the external magnetic field, and material gets magnetized. After the removal of external magnetic field, material still remains magnetized. That is a permanent magnet is produced. There is a temperature criterion to ferromagnetic material. That is after particular temperature material shows no ferromagnetic nature it becomes paramagnetic material and that temperature is Curie temperature. Susceptibility of ferromagnetic material is very hard  
Examples- Co, Ni etc.

### 4) Antiferromagnetic material: -

This type of materials has adjacent metal ions coupled with their spins antiparallel to each other. There are always equal and opposite number of alignments so that in the absence of magnetic field there is no magnetization. Susceptibility of antiferromagnetic materials is maximum at Neel temperature. In reality, antiferromagnetic order exists at sufficiently low temperature, but pernicious at and above certain temperature that is Neel temperature.

### 5) Ferrimagnetic material: -

Which type of materials have ions on two sets of lattice sites and they have opposite spin arrangement but this time the spin arrangement do not cancel each other because of the difference in the magnitude. Therefore, there is a resultant permanent magnetic moment in the direction of external magnetic field produced after it placed in the external magnetic field. Susceptibility of ferrimagnetic material is positive and high.

Examples-  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  etc.





### 1.3. Application of ferrites

1. Ferrites are mostly applicable in electronic products, automobiles, communication equipment's, data processing devices. Earlier, metallic magnets were used but for frequency greater than megahertz metals and alloys are not suitable as soft magnets as the Eddy current losses are generally very high. Another reason is resistivity of ferrites is million times greater than that of metals.
2. Soft ferrites or high frequency ferrites are used in radio, TV, microwave satellite communication, audio/video/digital recording as permanent magnets.
3. Hard ferrites are used as permanent magnets in speakers and micro motors.
4. Ferrites are used in telecommunications - ferrite cores are used on large scale and they are used to manufacture filter inductor, false and matching transformer.
5. Ferrite are used for power conversion generally in the form of switched mode power supply (SMPS)
6. Ferrites can be used to produce iron power ring cores, beads on wire, wideband chokes, cable shields, rod and tubes.
7. Magnetic sensors - ferrite can be used as temperature control sensors in which the sharp and definite Curie temperature is used in a temperature control sensor. Ferrites can also be used in position and rotational angle sensors or proximity sensors.
8. Magnetic shielding- Radar absorbing paint containing ferrites has been developed to render submarines.
9. Pollution control- The precipitate of ferrite precursor to scavenge pollutant materials such as Hg is used in various countries.
10. Ferrite electrodes- Ferrites with high corrosion resistance and appropriate conductivities are used in chromium plating.
11. Entertainment- Ferrites are used in radio and TV circuits as deflection yokes, flyback transformer and SMPS Transformers for power applications.





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## Chapter 2

### Theoretical Background of combustion by Micro-Oven method

Sr. No	Content	Page No
2.	Introduction	16
2.1	Microwave Assisted Synthesis	16-19
2.2	Background Details of Microwave Oven	20-28
2.3	References	29

## 2.Introduction

This chapter deals with the preparation method of metal oxide semiconductor like Ni-ZnFe<sub>2</sub>O<sub>4</sub> by microwave-assisted combustion method using different fuels (urea, glycine, carbonylhydrazide and citric acid). In the second section of this chapter, how microwaves interact with a material and why this interaction causes an increase in the temperature of the material are explained.

### 2.1. Microwave Assisted Combustion synthesis

Combustion synthesis is a high temperature synthesis in which an exothermic reaction is initiated in a mixture of powders. This exothermic process generates substantial heat, which can be utilized to produce ceramic powders. If the heat produced is very high, the product is porous and can be crushed easily to produce powders. In this method, urea is added as an ignitor to the mixed nitrate salt solutions. In some cases carbonylhydrazide (CH), tetraformyl trisazine (TFTA), maleic hydrazide (MH) or oxalyl dihydrazide are also used. This process yields reactive powders with extremely fine particle size, increased surface and possible low temperature sinterability (Sundar Manoharan et al 1992, Zhang et al 1994, Suresh et al 1994 and 1995, Ravichandran et al 1999, Ravindranathan et al 1987a and 1987b).



## CALCINATION

Powders often undergo a heat treatment (calcination). Calcination processes may be defined as endothermic reactions in which an oxysalt, such as a carbonate or hydroxide, decomposes leaving an oxide as a solid product and liberating a gas (Halloran 1991). Calcination is a convenient technique for producing finely divided and sinterable ceramic powders.

## MILLING

Milling is a size reduction process that occurs either by the particles impinging on each other, as in fluid energy milling, or by particles being compressed and sheared between the surfaces of wear-resistant milling media or the media and the mill lining.

## BINDER ADDITION

Some green strength is conferred on powders to be pressed by the addition of organic phases (binders) on mixing. All of these additions are usually fugitive and are removed on drying and sintering. The amount and type of additive may affect the extent of shrinkage and remnant porosity in the microstructure.

## PRESSING

In simple uniaxial dry pressing (actually contain 0-5% liquid) the granulated powder is placed in a die and pressure is applied to form the compact by crushing the granules and mechanical redistribution of the constituent particles into a close-packed array.

## DRYING

The packed powder compacts (samples) are placed for drying at 120°C to remove the moisture content.

## SINTERING

Sintering can be defined as densification, removal of the pores between starting particles accompanied by shrinkage of the component combined with growth together and formation of strong bonds between adjacent particles. Solid state sintering involves only solids and pores.





Products that have been dried and surface finished are called, "green products". The finished product requires firing treatment known as sintering in order to develop the desired microstructure and properties. This process called firing proceeds in three stages.

1. Reactions prior to sintering which include organic burnout and the elimination of decomposed gas product
2. Sintering
3. Cooling

Prior to sintering, the binder and the other additives in the powder compact have to be removed. Binder removal is accomplished thermally by heating the green body in high temperature. Thermal debonding of binder in ceramics is a complex process, which takes place in three different stages.

In the first stage of sintering, the binder present in the green body gets soft when the temperature reaches the range of 150-200°C. At this stage, chemical decomposition and binder removal are negligible. In the second stage of 200-400°C, most of the binder is removed by chemical decomposition. In the final stage, the small amount of binder still remaining in the powder compact is removed when the temperature reaches slightly above 400°C.

Sintering is the term used to describe the consolidation of the product during firing. Sintering gives strength to the shaped powders by joining the particles into an aggregate. During sintering, interparticle bond reduces the surface area, which in turn lowers the surface energy. The bonds grow by various mechanisms that occur at the atomic level. For many metals and ceramics, the bonding occurs by solid-state diffusion. Several reviews (Yan 1982, Handwerker 1988, Shaw 1989) give the details of solid-state sintering theory. Solid state sintering is usually employed in the case of single-phase material. Many of the sintering systems involve multiphases. The term liquid phase sintering describes the sintering process, in which a portion of the material, which is being sintered, is in liquid state. The formation of liquid phase during sintering usually increases the sintering rate and enhances the densification by particle rearrangement under the influence of capillary force and filling of pores.





Microstructural change during sintering takes place normally in three stages. Outlines the classic stages of sintering that represents the geometric progression involved in transforming the powder compact into a strong and dense component. Sintering usually occurs at temperature in excess, approximately one-half of the absolute melting temperature.

In the first stage of the sintering, the formation of grain boundaries causes the particles to join together. The degree of bonding in the initial stage ranges from point contact to highly deformed interface. The intermediate stage is the most important stage for densification and hence determines the properties of the sintered compact. The growing of neck is the focus of the initial stage of sintering. It loses its identity in the intermediate stage and the attention shifts to the pore volume, size, shape and the distribution. During this stage, the grain size increases. The pores attached to the grains coalesce (increase pore size) and the porosity is eliminated. Normally, the pores located on the grain boundaries shrink substantially faster than the isolated pores or the pores located in the interior of the grain.

When the grain growth occurs in the intermediate stage, pore migration and pore rounding occur due to active surface transport. As the pores shrink, the final stage of sintering occurs when the pore size/grain size ratio is small. If the grain growth is rapid in comparison with pore mobility, the pores are isolated from the grain boundaries, resulting in slow densification. Alternatively, if pore mobility is high, it disappears as it touches the grain boundary; it moves to new position and makes contact with the next layer of pores. Thus, the boundary begins to move slowly throughout the sample to sweep the region through which it moves free of pores which results in high densification. The sequence of pore isolation and spheroidization in the final stage of sintering is illustrated in. Microstructural changes in the final stages of sintering may proceed in a desirable or an undesirable manner. Many of the ferrite properties are highly dependent on processing parameters such as sintering temperature, sintering time, and heating atmosphere etc., as these parameters greatly influence crystal composition and size and also the size and volume of the pores. Many researchers have reported the electrical and magnetic properties of nickel-zinc ferrites with respect to sintering conditions.



## 2.2. BACKGROUND DETAILS OF MICROWAVE OVEN

Microwave technique has the potential to be a useful method for the preparation of nanoparticles. The potential advantages include more uniform temperatures in the sample, improved product uniformity, higher energy efficiency, less total time and space. Also, smaller grain sizes are achieved at any given density, leading to better and more uniform properties. A microwave oven works by passing non-ionizing microwave radiation, usually microwaves refer to the electromagnetic waves, in the frequency range of 300 MHz and 300 GHz (million cycles per second). Electromagnetic waves are waves of electrical and magnetic energy moving together through space. They include gamma rays, x-rays, ultraviolet radiation, visible light, infrared radiation, microwaves and the less energetic radio waves.

Ceramics are insulators; thus, electrons do not flow in response to an electric field. However, an electric field can cause a reorientation of dipoles, which can lead to heating. The rapidly changing electric fields associated with microwaves lead to rapidly changing orientations of the dipoles in the material. There is a natural frequency that causes maximum reorientation, thus maximum heating of the material. This is often referred to as "coupling". This is usually a very broad maximum, so that the frequency dependence is not strong. Each material has intrinsic properties relative to the absorption of microwave energy. Microwaves in this frequency range have another interesting property: they are not absorbed by most plastics, glass or ceramics and metal reflects microwaves. Because of the reflecting microwaves and infinite conductivity, no electronic waves resident inside of conductor. In a microwave oven, molecules of the sample are excited directly by the electromagnetic field; energy is absorbed by the sample, its temperature increases. The surface temperature becomes higher than the surroundings and loses heat by convection. Therefore, the surface temperature is lower than the core temperature. Because heat is being generated in the sample and conducted out of the sample, a stable temperature gradient can be achieved by applying constant power. Since conventional ovens lead to higher surface temperatures and microwaves lead to higher core temperatures, the right combination of the two could theoretically lead to equal core and surface temperatures. This would likely be a very





difficult combination to arrive at experimentally, because the combinations would change over a period of time. Also, the temperature would still probably not be constant throughout the entire sample, so the best-case scenario would be to minimize the temperature gradient to achieve the most even heating. Unlike conventional ovens, microwaves have "penetrating radiation, controllable electric field distributions, rapid heating, selective heating of materials through differential absorption and self-limiting reactions"

There are some potential problems with the use of microwaves. Materials with high electrical conductivity generally are difficult to process because of poor penetration of the microwave energy. Insulators with low dielectric loss are hard to heat because of poor absorption of microwave energy. Some materials are highly temperature dependent dielectric properties, often causing uneven heating and thermal runaway.

In recent years, extensive research has been done in the area of microwave processing of nanoparticles. Part of the reason for the increase in study in this area is the expectation of different and perhaps better, properties than those achieved in traditional convection ovens. The fact that microwaves heat materials by internal absorption that resembles heat generation makes uniform heating and thus uniform properties. Experimental evidence shows that uniform heating is not achieved, and very large temperature gradients can result. This is caused by the loss of heat due to convection at the surface. The nonuniformity is then compounded by the temperature dependence of the absorption of microwave energy, which increases with temperature in some materials.

Ni-Zn ferrites are magnetic ceramic materials composed of metal oxides with iron oxide as their main constituent. These ferrites have now been firmly established as one of the most important classes of magnetic materials and are indispensable in Electrical, Electronics and Communication Engineering for a variety of high-performance applications such as chip inductors, transformers, choke coils and electromagnetic absorbers. These applications require high quality, ultra-pure and fine-grained materials. The application of novel wet chemical methods like flash combustion and citrate-gel decomposition techniques to Ni-Zn ferrites technology brings new possibilities in synthesizing high purity Ni-Zn ferrites at relatively low

temperatures. These techniques yield Ni-Zn powder with desired size, shape, size distribution, chemical homogeneity and high purity powders. In the present investigation, a systematic study was carried out in the preparation techniques of extremely pure Ni-Zn ferrite powder and its powder characteristics, sintering studies, microstructure, magnetic, electrical, dielectric and mechanical properties for use at high frequency applications with high resistivity and low losses. The corresponding metal nitrate salts were used as the starting materials for the preparation of  $Ni_{1-x}Zn_xFe_2O_4$  (where  $x = 0.2, 0.3, 0.4, 0.5$ ) powders. In flash combustion techniques; urea was used as ignitor and it was allowed to decompose at  $500^\circ\text{C}$ . At that temperature the metal nitrates and urea reacted giving out gases and the combustion was completed in 3-5 minutes, yielded a foamy and highly porous (fluffy nature) precursor mass. It was then powdered for further processing.

The particle size analysis of Ni-Zn ferrites prepared by these techniques shows a narrow particle size distribution. Due to exothermic reaction, during combustion, the reactants are exposed into a reactive mixture. This was given a marginal value of about 2% weight loss in both techniques. The formation of a single spinel phase was confirmed by XRD patterns. The crystallite size was studied using XRD, which showed that the crystallite size of Ni-Zn ferrite for Microwave assisted technique was 45-60 nm and 80-95 nm respectively.

The precursors calcined at  $900^\circ\text{C}$  for 2 hrs were dry milled to avoid agglomeration. 2.0 wt% of PVA was used as a binder for granulation and good compaction. Then the powders were compacted into pellets and toroids. The fabricated samples were dried at  $110^\circ\text{C}$  for 24 hrs to remove the moisture. The dried samples are then sintered at sintering temperature such as  $1150^\circ\text{C}$  for 3 hrs. The sintered properties such as bulk density and porosity were determined using Archimedes principle. It was observed that the sintered density increases with Zn substitution and also with sintering temperature. The percentage porosity in the range between 13.7-27.2 for microwave assisted technique. The magnetic properties of Ni-Zn ferrites are known to be influenced by chemical composition, crystal structure, grain size and porosity. It was observed that for all compositions the initial permeability was independent of frequency and increased with sintering temperature. The increase in the sintering temperature results in a decrease in the magnetic anisotropy by decreasing the internal stress and crystal anisotropy, which reduces the hindrance to the movement of the domain walls thereby resulting in the increased value of the initial permeability. The low permeability loss of the order of





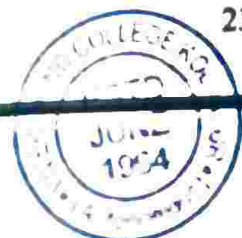
$10^3-10^4$  was obtained for all compositions of Ni-Zn ferrite samples. It has been reported that ferrites prepared by conventional ceramic method have the permeability loss possess values of the order of  $10^2$ . The low value obtained in the present work indicated that the samples were relatively pure. The initial permeability/temperature relation showed that the Curie temperature decreases with zinc concentration and was in agreement with the literature values. The coercivity obtained was in the range between 3.794 and 7.870 Oe.

The AC electrical resistivity ( $\rho_{ac}$ ) of the order of 105 Qcm was obtained for all compositions at 10 kHz. This was in accordance with the observed results earlier. High DC electrical resistivity values ( $\rho^d$ ) of the order of 108-109 Qcm were observed for all compositions at room temperature. This was higher than that of the reported values of Ni-Zn ferrites prepared by conventional ceramic method. It has been reported that the resistivity of a polycrystalline material in general increases with decreasing grain size. The low values of dielectric constant and dielectric loss obtained were due to the greater structural homogeneity and molecular level of mixing of starting materials used in the preparation of ferrites. Higher porosity and lower density result in lower dielectric constant and dielectric loss. Since there is a strong correlation between the dielectric constant behavior and the resistivity of the ferrites, the high resistivity values observed in the present work confirms that the dielectric constant of the Ni-Zn ferrite samples should be low.

A highest hardness value of 3.63 GPa were obtained for Ni-Zn ferrite prepared by microwave assisted technique. The values of sintered density and porosity obtained greatly influence the mechanical properties of Ni-Zn ferrites. The microstructure and fracture surface analysis were carried out for all the samples to investigate the grain growth morphology. It is observed that higher porosity and smaller grain size observed in the present work lead to high resistivity and low loss.

### MICROWAVE-ASSISTED COMBUSTION SYNTHESIS

Two important aspects of microwave assisted combustion synthesis are its instantaneous and volumetric heating characteristics. Therefore, the entire mixture reacts uniformly throughout, at the moment of heating. Microwave heating has other advantages as well. The heating is outward from the center, giving rise to inverse temperature gradients. This can lead to different microstructures. Also, since the heating is instant, microwave power can be used to control the



extent of reaction. The potential of microwave heating to control the extent of the reaction and possibly yield Nano-overlayers of ceramic on metal substrates can be explained as follows. Microwave energy can interact with metal powders as well as non-metals. The power absorbed per unit volume (W/m<sup>3</sup>) provides the following basis for heating.

$$P = \sigma |E|^2$$

Where  $\sigma$  = total effective conductivity =  $2\pi f \epsilon_0 \epsilon_r \tan \delta$

$E$  = local electric field

$f$  = frequency of microwave

$\epsilon_0$  = permittivity of free space

$\epsilon_r$  = relative dielectric constant

$\tan \delta$  = loss tangent =  $\epsilon''/\epsilon'$

where materials complex permittivity =  $\epsilon^* = \epsilon' - i\epsilon''$

Since the effective conductivity  $\sigma$  for metallic samples is 10<sup>6</sup> to 10<sup>16</sup> higher than for non-metal dielectric materials, at 2.45 GHz the skin depth for metallic samples is sometimes a few micrometers or less. Hence the absorption of microwave energy is a relatively thin outer layer, which then transmits energy by conduction to inner layers. "The heating of metals is attributed to eddy current losses from the magnetic fields". The demonstrated heating of metal particles by microwaves lead to the following hypothesis, since the heating of the metals is limited to a thin surface layer the probability of reaction with a non-metal at this surface layer is at maximum and would lead to a ceramic over layer formation. Furthermore, since microwave heating is instantaneous, switching the microwave on or off can control the reaction. Thus switching the microwave on would lead to reaction and if the reaction has not reached the self-sustaining stage, switching the microwave off would stop the reaction. For reactions that would not be self-sustaining because of a very low adiabatic flame temperature, microwave energy may also be used to drive these reactions at stoichiometric conditions. For reactions having a low flame temperature because of extremely low concentration of one reactant, microwave heating may also be used to promote reaction



## Principles of Microwave Oven

Microwaves are a form of energy which is absorbed, polar molecules and ions inside the sample will rotate or collide according to the alternating electromagnetic field and heat is subsequently generated for preparation of nanoparticles. Microwaves make the water molecules inside the sample vibrate so that they rub against each other causing friction. These frictions produce the heat that actually makes the sample. Energy → Vibration → Friction → Heat → Sample In a microwave the heat is produced inside the sample. Microwave energy penetrates the sample to a depth of about 25 mm. Microwaves are similar to light and they are emitted downwards from the top of the microwave oven cavity. The waves bounce off the metal sides of the cavity, hitting the sample from different angles. These microwaves do not hit the sample evenly. To minimize this effect, the oven either has a rotating turntable or a paddle wheel in the roof to stir up the microwaves.

### WORKING PRINCIPLES OF MICROWAVE OVENS

In a microwave oven, sample is heated by exposing it to microwave radiation. The source of the radiation in a microwave oven is the magnetron tube. The heart of a microwave oven is the magnetron. A magnetron converts electrical energy into microwave radiation. To do this, it uses low-voltage alternating current and high-voltage direct current. A transformer changes the incoming voltage to the required levels and a capacitor, in combination with a diode, filters out the high voltage and converts it to direct current. Inside the magnetron, electrons are emitted from a central terminal called a cathode. A positively charged anode surrounding the cathode attracts the electrons. Instead of traveling in a straight line, permanent magnet forces the electrons to take a circular path. As they pass by resonating cavities, they generate a continuous pulsating magnetic field, or electromagnetic radiation. The microwave energy from the magnetron is transferred to the oven cavity through a waveguide section. A mode stirrer spreads the microwave energy more or less evenly throughout the oven. The microwave radiation produces heat inside the sample kept in the oven. Heat is produced when the water molecules in the sample vibrate (at a rate of 2.45 GHz) when the sample absorbs the microwave radiation. The movement of the molecules produce friction which causes heat. This heat produces the nanoscale





materials. Microwave radiation is measured as power density in units of milliwatts per square centimeter ( $\text{mW}/\text{cm}^2$ ) which is essentially the rate of energy flow per unit area.

### DETAILS ABOUT THE MICROWAVE OVEN

A microwave oven can be divided into two fundamental sections, the control section and the high-voltage section. The control section consists of a timer (electronic or electromechanical), a system to control or govern the power output and various interlock and protection devices. The components in the high-voltage section serve to step up the house voltage to high voltage. The high voltage is then converted into microwave energy.

The working of the oven i.e electricity from the wall outlet travels through the power cord and enters the microwave oven through a series of fuse and safety protection circuits. These circuits include various fuses and thermal protectors that are designed to deactivate the oven in the event of an electrical short or if an overheating condition occurs. If all systems are normal, the electricity passes through the interlock and timer circuits. When oven door is closed, an electrical path is also established through a series of safety interlock switches. Setting the oven timer and starting the operation extends this voltage path to the control circuits. Generally, the control system includes either an electromechanical relay or an electronic switch called a triac. Sensing that all systems are "go," the control circuit generates a signal that causes the relay or triac to activate, thereby producing a voltage path to the high-voltage transformer.

By adjusting the on-off ratio of this activation signal, the control system can govern the application of voltage to the high voltage transformer, thereby controlling the on-off ratio of the magnetron tube and therefore the output power of the microwave oven. Some models use a fast-acting power-control relay in the high-voltage circuit to control the output power.

In the high-voltage section, the high-voltage transformer along with a special diode and capacitor arrangement serve to increase the typical household voltage, of about 115 volts, to the shockingly high amount of approximately 3000 volts! While this powerful voltage would be quite unhealthy - even deadly - for humans, it is just what the magnetron tube needs to do its job,





i.e. dynamically convert the high voltage into undulating waves of electromagnetic energy. The microwave energy is transmitted into a metal channel called a waveguide, which feeds the energy into the working area where it encounters slowly the revolving metal blades of the stirrer blade. Some models use a type of rotating antenna while others rotate the materials through the waves of energy on a revolving carousel. In any case, the effect is to evenly disperse the microwave energy throughout all areas of the working compartment. Some waves go directly toward the materials, others bounce off the metal walls and flooring and microwaves also reflect off the door. So, the microwave energy reaches all surfaces of the material from every direction. All microwave energy remains inside the working cavity. When the door is opened, or the timer reaches zero, the microwave energy stops-just as turning off a light switch stops the glow of the lamp.

### **MICROWAVE HEATING**

The absorption of microwaves by a material results in the microwaves giving up their energy to the material. This transfer of energy causes the temperature of the material to rise. The microwaves themselves do not heat up the materials. The heat generation in a microwave field is caused by ionic polarization and dipole rotation of the water molecule.

Molecules of all samples consist of a dipole and have positive charge in one side and have negative charge in another side. If we put electromagnetic fields in this, all molecules are rearranged: positive charge is to negative pole and negative charge is to positive pole. In this process heat is produced by friction. The frequency of microwave oven is 2,500 MHz as we saw before. Then microwave of this frequency change the direction of electromagnetic fields 2.5 GHz times in 1 second. Consequently, the heat efficiency of a microwave oven is greatly high.

A polar molecule in the presence of microwave field attempt to orient themselves according to the rapidly changing field. The rotation of the molecule leads to friction with surrounding medium and heat is generated. The rotation of the molecule also produces kinetic energy, which produces additional heat. Ionic conduction is another important microwave heating mechanism. When an electrical field (i.e. microwave field) is applied to solutions containing ions, the ions move at an accelerated pace due to their inherent charge. The ions collide and the collisions



cause the conversion of kinetic energy of moving ions into thermal energy. A solution with higher concentration of ions will have more frequent collisions and therefore heat transfer faster than a solution with lower concentration.



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## Chapter 3

### Literature Survey

Sr. No.	Content	Page No.
3.1	Literature Survey	30-32
3.2	Reference	33

### 3.1. Literature Survey of Ni-Zn Ferrite

In recent years, the researchers strongly focused on the synthesis of nanosized (nanocrystalline) Nickel-Zinc Ferrite by the solution combustion method and microwave-assisted combustion method. Using this method, the heating and evaporation of metal nitrate solution with an organic compound like fuels (such as glycine, urea, carbonylhydrazide, citric acid etc.) results in self-firing and generates intense heat by exothermic reaction. This intense heat is used to synthesize the Nano powders. This novel approach has the advantages of inexpensive raw materials, a relatively simple preparation process and a fine resulting powder with high homogeneity. Microwaves have been used for applying microwave irradiation to chemical reactions. Microwaves act as a high frequency electric field generator and will generally heat anything with a mobile electric charge. Polar solvents are heated as their component molecules are forced to rotate with the field and lose energy in collisions. Semiconducting and conducting samples heat when ions or electrons within them form an electric current and energy is lost due to the electrical resistance of the material. Heating a reaction or chemical reactor by microwave radiation (as seen in a domestic microwave oven) has several advantages over conventional heating.

Ferrites are mostly prepared via conventional ceramic processing involves commercially both long and high temperature treatments for the oxides used in their preparation. Ni-Zn ferrites having spinel crystal structure are extensively used in a number of electronic devices because of their high permeability at high frequency, remarkably high electrical resistivity, mechanical hardness, chemical stability, and reasonable cost. Zn and Ni are known to have very strong preferences for the tetrahedral and octahedral sites, respectively, making Ni-ferrite a model inverse ferrite and Zn-ferrite a model normal ferrite. This system has been extensively studied





for various properties as well as for structural issues.

The studies on magnetic and dielectric properties in Ni-Zn ferrites synthesized by conventional technique have been reported by so many workers. The conventional method is the most common method for preparing ferrites for so decades. They investigated the frequency, temperature and composition dependence of Ni-Zn ferrites. They suggested the variation of dielectric constant depends linearly on the variation of available ferrous ions on octahedral sites. Dielectric constant declined with increasing frequency. The maximum dielectric dispersion was seen which be explained on the basis of available ferrous ions on octahedral sites.

The variation of the dispersion with composition for mixed nickel-zinc ferrites was explained by the fact the electron exchange between  $Fe^{2+}$  and  $Fe^{3+}$  in an n-type semiconducting ferrite and hole exchange between  $Ni^{3+}$  and  $Ni^{2+}$  in a p-type semiconducting. They measured resistivity and dielectric constant was inversely proportional to the square root of resistivity. Additionally, the dielectric loss reflected in resistivity that the lower loss exhibited higher resistivity and vice versa. In their research the dielectric constant increased gradually with increasing temperature up to the particular temperature, which is designated as the dielectric transition temperature  $T_s$ . However, beyond this temperature the values of the dielectric constant for all the samples were found to decrease continuously.

The conductivity of  $Ni_{1-x}Zn_xFe_2O_4$  as a function of composition and temperature. They observed conductivity increase with zinc content and temperature. They calculated the charge carrier concentration and observed the higher charge carrier in higher temperature up to magnetic transition temperature. Beyond this temperature the concentration of charge carrier decreased. The electrical conductivity of  $Ni_{1-x}Zn_xFe_2O_4$  ( $x = 0.1, 0.3, 0.5, 0.7$  and  $0.9$ ) which were prepared by the ceramic processing technique. They found the lowest conductivity and higher activation energy for  $x=0.3$  in nickel zinc ferrite.

The substitution of Zn in the  $Ni_{1-x}Zn_xFe_2O_4$  system and checked the effect on the physical properties. They studied the variation of zinc content on DC resistivity, dielectric constant and loss factor. It was observed that dielectric constant increased with the increase in Zn



concentration. The resistivity values were in the range of  $1.629 \times 10^6$  to  $3.0 \times 10^3$   $\Omega\text{cm}$ . Loss factor remained in the range of 0.057–0.456 with the variation in frequency from 80 Hz to 1 MHz, respectively. It is observed by various workers that the magnetization having the highest values for  $x = 0.3$ – $0.4$  in  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ . So, it was decided that it will be very interesting to conduct the further research with different ion substitution by keeping  $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$  as a parent compound.

In conventional methods, there are some inherent drawbacks such as poor compositional control, chemical inhomogeneity, coarser particle and introduction of some impurities during milling. Thus, the coarser and non-uniform particles cause the formation of some voids and low-density areas in the green compact. However, the variety wet methods such as ball milling, hydrothermal, sol-gel, microemulsions, and co-precipitation have been used to synthesize ferrite materials. Each method has unique advantages. But trying to improve the physical properties of ferrites by new designing in synthesize is still a matter of primary interest. Recently sol-gel methods have been used to prepare ultrafine, homogenous and reproducible powder. In the recent past, the sol-gel method has been found to have distinct advantages over the conventional dry processing. The final goal is to fabricate the ferrites with better physical and magnetic properties that are useful in a variety of industrial applications.



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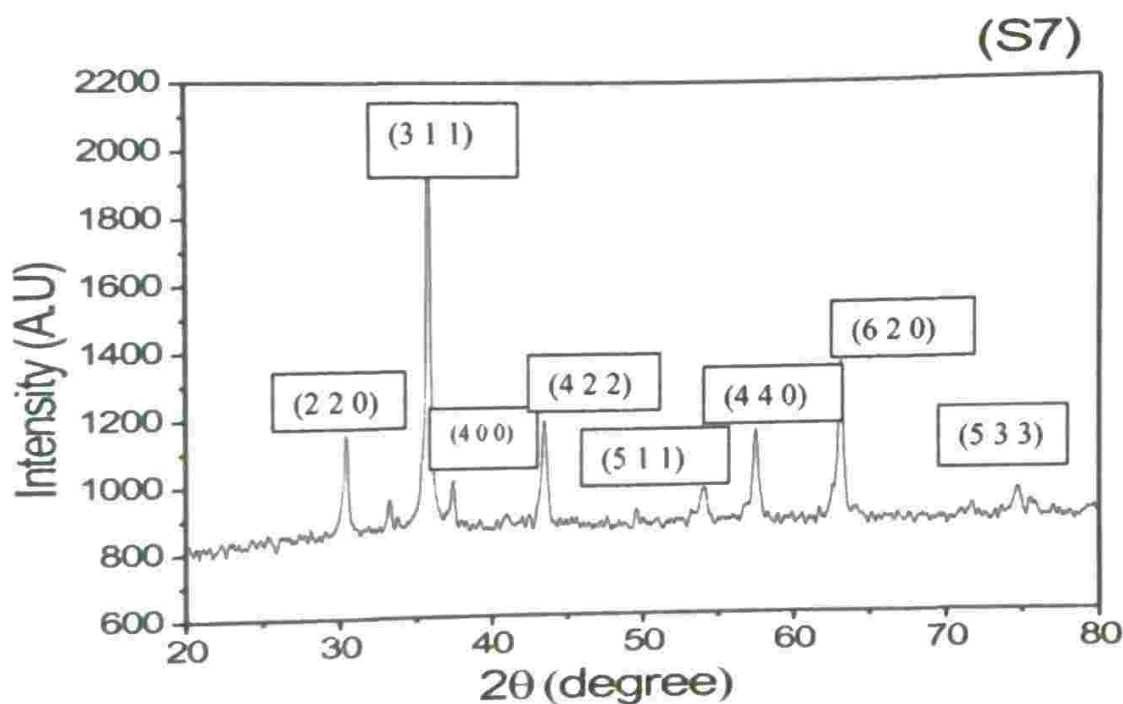




## Chapter 4

### Synthesis and Result

Analytical grade nickel nitrate hexahydrate ( $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, >97\%)$ , ferric nitrate nonahydrate ( $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}, >98\%)$ , zinc nitrate hexahydrate ( $(\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, >99\%)$ , and urea ( $\text{CO}(\text{NH}_2)_2$ ) were used without further purification. An appropriate ratio of nickel nitrate, zinc nitrate (according to the  $x$  in  $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ) ferric nitrate, and urea -to serve as fuel, were dissolved in deionized water and poured into a crucible, which was then placed in a kitchen-type microwave oven at a maximum power of 800W for 5min. The solution initially boils then undergoes dehydration followed by decomposition with the evolution of large amount of gas. When the solution reaches the point of spontaneous combustion, it begins to burn by releasing lots of heat, vaporizes all the solution instantly and turns into a solid, thus forming the desired phase.

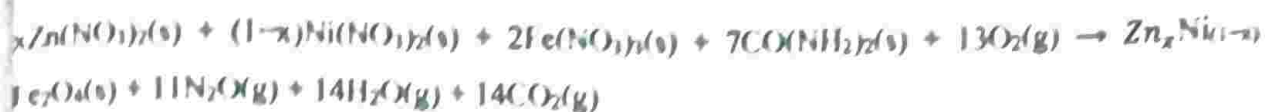


In order to investigate the crystal structure of the obtained powder material XRD analysis was performed and the resultant pattern of the as-prepared sample is presented in the above figure. The analysis of the diffraction pattern by using (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (6 2 0), and (5 3 3) reflection planes confirm the formation of cubic spinel structure. No secondary phase was detected in XRD which ensured the phase purity of the final product. The entire combustion reaction takes place in only 5 min to produce  $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$  powders in a microwave oven.





The reaction can be described as follows:



To determine the crystallite size of the samples, the XRD profiles were fitted according to the Equation in which allows the estimation of average crystallite size and its standard deviation from XRD. The experimental line profiles, shown in the above figure, were fitted for the observed 8 peaks (reflection planes).

Chemical compositions of samples were confirmed. Based on this composition then we attempted to calculate the lattice constants for the three investigated systems. The lattice constant for each peak for each sample was calculated using the data from the observed diffraction planes. In order to determine the exact lattice parameter for each sample, Nelson-Riley function,  $F(\theta)$ , was used where  $F(\theta)$  is given as  $F(\theta) = 1/2[(\cos^2\theta/\sin\theta) + \cos^2\theta/\theta]$ . The values of lattice constant  $a_0$  of all the peaks for a sample were plotted against  $F(\theta)$  (data not shown). Then using a least square fit method, exact lattice constants  $a_0$  were calculated as presented. The point where the least square fit straight line cuts the y-axis (where  $F(\theta) = 0$ ) is the actual lattice parameter of the composition. The increase in  $a_0$  with increase in Zn content also suggested the formation of a compositionally homogeneous solid solution as

$a_0$  was found to be within the range of the lattice constants of  $\text{ZnFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  (JCPDS Card No. 89-1012, with  $a = 8.433\text{\AA}$  for  $\text{ZnFe}_2\text{O}_4$  and JCPDS Card No. 22-1086 with  $a = 8.381\text{\AA}$  for  $\text{NiFe}_2\text{O}_4$ , respectively).

This increase could be also attributed to the substitution of small Ni cations (0.78 Å) with larger Zn cations (0.82 Å) larger  $\text{Zn}^{2+}$  replacing  $\text{Ni}^{2+}$  ions therefore causing the crystal to slightly expand in agreement with the Vegard's law.



From the extrapolation of curve, lattice parameter for  $\text{ZnFe}_2\text{O}_4$  is obtained as 8.46Å which confirms a linear expansion of the crystal by  $\text{Zn}^{2+}$  substitution. This value is in agreement with that given in the ICDD Card No: 89-1012 for  $\text{ZnFe}_2\text{O}_4$  as also described in our previous study.



## Chapter 5

### SUMMARY

The development of ceramic processing techniques has brought the hope of producing ultra-fine and ultra-pure powders with appreciable properties. The non-conventional methods adopted in this work namely Microwave Assisted techniques are simple and do not require elaborate instrumental set-up. The ferrite materials prepared by these techniques are pure, and highly reactive because of the atomic level mixing of the starting materials. The ferrites prepared by these methods are have better microstructure and high chemical homogeneity, which result in good magnetic, electrical, dielectric and mechanical properties. Also, it is possible to obtain controlled grain growth with relatively uniform grain size.

In the present work, Ni-ZnFe<sub>2</sub>O<sub>4</sub> Nano powders were prepared by an efficient and simpler way, using low temperature, cost effective, large scale production, rapid and fast. They are the main requirement for this microwave-assisted combustion method. However, it is a challenge to find a prepared powder with particle size about few nanometers through this method. Therefore, the study of the influence of various process parameters such as initial solution combination using fuels, time and temperature of heat treatments are very important for the preparation of Nano powders. All the powders are prepared using various organic fuels like urea, glycine, carbonylhydrazide and citric acid in stoichiometric (fuel-to-oxidizer) molar ratios. The as-prepared powders and different treated temperature were characterized by XRD. The structural, morphological, optical, electrical and gas sensing characters were studied. The ethanol sensing property of Ni-ZnFe<sub>2</sub>O<sub>4</sub> were studied for their sensitivity and stability.

The Ni-ZnFe<sub>2</sub>O<sub>4</sub> powders were synthesized by adding the fuel in stoichiometric equilibrium ( $\Phi=1$ ) based on the thermochemical concepts of propellant chemistry calculation of fuel-oxidant mixtures. The effects of various organic fuels and different treated temperatures on crystalline phase formation, particle size and its structure have been investigated. The synthesized Ni-ZnFe<sub>2</sub>O<sub>4</sub> Nano powders were characterized through powder X-ray diffraction and they were found polycrystalline for all the fuels with various treated temperatures.



The structure refinement by Rietveld method was done for the powder X-ray diffraction pattern of the various organic fuels used Ni-ZnFe<sub>2</sub>O<sub>4</sub> Nano powders with different treated temperatures and the results are discussed.

High values DC-resistivity ( $\rho_{dc}$ ) of the order of 108-109 Qcm is obtained for ferrites prepared by these methods. The AC-resistivity ( $\rho_{ac}$ ) decreases as the frequency increases which is exhibiting the normal behavior of ferrites. High  $\rho_{ac}$  of the order of 105 Qcm is obtained at 10 kHz in the room temperature. The increasing sintered density with increase in Zn substitution is evident that the reduced value of resistivity of Ni-Zn ferrites as the Zn concentration increases.

The dielectric constant and dielectric loss factor of Ni-Zn ferrite samples prepared by Microwave Assisted techniques were studied as the function of frequency and sintering temperature.

The dielectric constant ( $\epsilon'$ ) and dielectric loss factor ( $\tan\delta$ ) decrease as the frequency increases, which are also exhibiting the normal behavior of ferrites. The  $\epsilon'$  and  $\tan\delta$  observed in the present work are lower than that of reported values of Ni-Zn ferrites prepared by conventional ceramic method. The increase in Zn substitution decreases the values of  $\epsilon'$  and  $\tan\delta$ .

The microstructure analysis was studied for Ni-Zn ferrite samples of different compositions sintered at various sintering temperature. The grain size of the order of 2-4, 4-7 and 8-12 pm is obtained for Ni-Zn ferrite samples prepared by these Microwave Assisted techniques and sintered at 1150°C respectively. High quality ferrites can be prepared by these non-conventional techniques, which give better microstructure and high chemical homogeneity. The surface microstructure of zinc bearing ferrites has some degree of duplex microstructure due to zinc evaporation.





## CONCLUSIONS

- The  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.2, 0.3, 0.4$  and  $0.5$ ) powders were successfully prepared by Microwave Assisted techniques.
- The powder characteristics analysis by XRD were analyzed.
- The physical properties, bulk density and porosity of different compositions of Ni-Zn ferrites sintered at  $1150^\circ\text{C}$  were studied.
- The properties of the Ni-Zn ferrites obtained by Microwave Assisted techniques were compared with the reported values of the Ni- Zn ferrites prepared by conventional ceramic method.



## PROPOSALS FOR FUTURE RESEARCH

Our work does not end here. The implementation of the nanoscopic techniques pave new ways and create highly interesting in the nanomaterials field. The most direct application will be the analysis of samples obtained with new and more "exotic" materials and study the new characteristics of the nanomaterials. In this way, we have started to prepare and characterize new samples made from different metal oxide semiconductors powders by microwave and solution combustion method.

Further research effort should be made to enhance the understanding of additional characteristics of the multi-component of Nickel Zinc Ferrite. The detailed study of additional experimental parameters had significant effect on the nanomaterial properties such as various powers of microwave heating and the different treated temperatures in various other atmospheres with improved characteristics.



# **SYNTHESIS OF MnO<sub>2</sub> THIN FILM BY ELECTRODEPOSITION TECHNIQUE**

A Dissertation Report Submitted to

**Vivekanand College (Autonomous),**

**KOLHAPUR.**

**For the Partial Fulfillment of  
Degree of Master of Science**

In

**PHYSICS**

**Under the Faculty of Science**

by

**Mr. PATHAK ONKAR HERAMBRAJ**

B.Sc.

**Under the Guidance of**

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**M.Sc., Ph.D.**

**Department of Physics,  
Vivekanand College (Autonomous),  
Kolhapur.  
2018-2019**





## DECLARATION

I hereby declare that, the project entitled "**Synthesis of MnO<sub>2</sub> Thin film by Electrodeposition**" completed and written by me has not previously formed the basis for the award of any Degree or Diploma or other similar title of this or any other University or examining body.

**Place:** Kolhapur

**Date:** 29/03/2019

*Pathak*

**Mr. PATHAK ONKAR HERAMBRAJ**

**B.Sc. (Physics)**



# CERTIFICATE

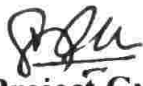
This is to certify that the project entitled "Synthesis of MnO<sub>2</sub> Thin film by Electrodeposition" which is being submitted herewith for the award of the Degree of Master of Science in Physics of Vivekanand College (Autonomous), KOLHAPUR, is the result of the original project work completed by Mr. PATHAK ONKAR HERAMBRAJ under our supervision and guidance and to the best of our knowledge and belief the work embodied in this project has not formed earlier the basis for the award of any Degree or similar title of this or any other University or examining body.

Place: Kolhapur


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2018-2019



## ACKNOWLEDGEMENT

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I have great pleasure to express my deep sense of indebtedness and heart full gratitude to **Dr. M. M. Karanjkar**, Professor, Department of Physics, Vivekanand College (Autonomous), Kolhapur, for his expert and valuable guidance and continuous encouragement given to me during the course of my project work. He has already been a source of strength for me. I find in him a real researcher who through his own example and devotion for scientific work inspired me towards a common goal of achieving scientific knowledge and pursuit.

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My acknowledgement will be incomplete if I don't express my appreciation towards my family members whose good will & inspiration helped us a lot in completing this project work.

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**B.Sc. (Physics)**





# INDEX

<b>Sr. No</b>	<b>Content</b>	<b>Page No</b>
<b>1.</b>	<b>Introduction</b>	<b>6-13</b>
<b>2.</b>	<b>Theoretical Background</b>	<b>14-28</b>
<b>3.</b>	<b>Literature Survey</b>	<b>30 33</b>
<b>4.</b>	<b>Synthesis &amp; Result of MnO<sub>2</sub> Thin Film</b>	<b>34-39</b>
<b>5.</b>	<b>Summary &amp; Conclusion</b>	<b>43-44</b>



**CHAPTER 1**  
**INTRODUCTION**

<b>Sr. No</b>	<b>Content</b>	<b>Page No</b>
<b>1.1</b>	<b>Introduction to Thin films Technology</b>	<b>7</b>
<b>1.2</b>	<b>Deposition Technique</b>	<b>10</b>
<b>1.3</b>	<b>Basics of Electrodeposition</b>	<b>12</b>
<b>1.4</b>	<b>References</b>	<b>13</b>



## 1.1 Thin Film : An Introduction

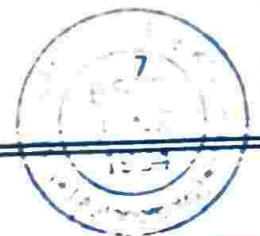
A thin film is a layer of material ranging from fraction of a nanometre to several micrometers in thickness. Thin films have been used in the study of the relationship between the structure of solids and their physical properties. Practical applications include electrical circuits, optical instruments and magnetic information storage devices. Thickness of the thin film is usually discussed in terms of angstrom units (Å). Thin films are formed by depositing material onto a clean supporting substrate to build up film thickness, rather than by thinning down bulk material.

“A surface bounded between two parallel plane extending infinitely in two directions restricted in the dimension along third direction.”

OR

“Any solid or liquid system possesses at most two-dimensional order or periodicity is called as thin film”.

Many of the electric semiconductor devices are the main application benefiting from thin film construction. The semiconducting material, in thin film form are of particular interest because it has a various number of applications like transparent electrodes, photovoltaic devices, solar front panel display, surface acoustic wave devices, low emissivity coating for architectural glass, various gas sensors and heat reflectors for advanced gazing in solar cells. A familiar example is the household mirror which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors, while more recently the metal layer is deposited using techniques such as sputtering. During the 20<sup>th</sup> century there are some industrial areas the thin film technique was used such as magnetic recording media, electronic semiconductor devices, LED's, optical coatings, like antireflective coatings, hard coatings on cutting tools. It is also applied to pharmaceuticals, thin film drug delivery; a stack of thin films is called multilayer. Due to surface and interface effects: properties of thin film differ considerably from those of bulk and this will dominate overall behaviour of the thin films. Thin films play an important role in the nanotechnology and nanoscience development. Now days, Solar cell is an important application of thin film technology, which converts the energy of the light energy to the electrical energy. The thin solid films were probably first obtained by





electrolysis in 1838. The conventional bulk material is characterized by three dimensional order in which the constitute atoms or molecules find themselves. This order or periodicity is responsible for the structure/nature of the material, which in turn is at the heart of distinct physic-chemical properties of the materials. In case of thin films, the system possesses at most two-dimensional order or periodicity. This accounts for the vast difference in physic-chemical properties between bulk material and its thin film counterpart. Applications of thin film technology have revolutionized the field of optics, electronics, sensors,

In the thin film technology there various types of substrates were used like Glass Substrate, Steel substrates, copper substrate etc. Thin film deposition techniques a large number of deposition techniques are used to deposit the thin films. There are two main & most important types of the deposition techniques are

### ▪ Physical Vapour Deposition (PVD)

In each techniques appropriate coating of materials are mandatory, in Physical deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film of sold. A day to day example is the deposit of small white ice crystals formed on the ground or plant leaves or other surface when the temperature falls below freezing. The whole system is kept in a vacuum deposition chamber to allow the particles to travel as freely as possible, since particles tend to follow a straight path films deposited by physical means are directional rather than conformal .

Examples of physical deposition include: - A thermal evaporator that uses an electric resistance heater to melt the material and raise its vapour pressure to a useful range. This all process is proceeding in high vacuum. In this process only materials can be deposited which having a much higher Vapour pressure than the heating element. In the PVD there are many types of evaporation techniques like

- Electron beam evaporation- a highly energies beam fires from an electron gun & which to boil a small spot of material. By using EBE lower vapour pressure materials can be deposited. The beam is usually bent through an angle of  $270^\circ$  . We have to ensure that the gun filament is not directly exposed to the evaporant flux.
- Sputtering this process is done by the particles are ejected from a solid target material due to bombardment of the high energy particles on the target. It happens only when the kinetic energy of the incoming particles is much higher than conventional thermal energies. Sputtering relies on plasma usually a noble gas such as argon. The target can

be kept at relatively low temperature since the process is not one of evaporation making this one of the most flexible deposition techniques. The sputtering technique is widely used in the optical media. The manufacturing of all formats of CD, DVD is done with the help of this technique. It is fast technique and it also provides a good thickness control.

## Chemical Vapour Deposition (CVD)

- In the chemical vapour deposition technique for each deposition chemical is used for deposition of thin films. CVD process use of dip coating and spinning, liquid inorganic and organic compounds and gases.
- In the CVD by using two different phases we can deposit the thin films.. The two phases are GAS PHASE & LIQUID PHASE. In the gas phase the inert gases are used for the deposition and in liquid phase precursor solution i.e. liquid solution is used for the deposition.
- Dip coating is similar to the spin coating in that sol-gel is used for the precursor. (Liquid precursor). We can control the speed for the homogeneity.
- In the CVD technique the various types of deposition method like Laser Vapor Deposition, Photochemical Vapor Deposition, Plasma-enhanced chemical vapour deposition & metal organochemical vapour deposition All of this types are in gas phase
- In the liquid phase there are Chemical Bath Deposition, Successive Ionic Layer Adsorption and Reaction (SILAR), Sol gel Process, Spray Pyrolysis & electrodeposition

Liquid compounds and gases are normally purchased directly from the producer, because it needs no special preparation.



## 1.2 Deposition techniques

The wide classification of the thin film deposition techniques are listed below. All these thin film deposition techniques electrochemical deposition offers a wide range of advantages over more expensive and vacuum based other method of thin film all of methods having some advantages like no wastage of material, no any production of gases, it does not require very starting material etc





# Thin Film Deposition Techniques

## Physical

### Vacuum evaporation

- ❖ Resistive heating
- ❖ Electron beam evaporation
- ❖ Flash evaporation
- ❖ Laser evaporation
- ❖ Arc evaporation
- ❖ Radio frequency (RF) heating

### Sputtering

- ❖ Glow discharge DC sputtering
- ❖ Getter sputtering
- ❖ Triode sputtering
- ❖ Radio frequency (RF) sputtering
- ❖ Magnetron sputtering
- ❖ Face target sputtering
- ❖ AC sputtering
- ❖ Ion beam sputtering

## Chemical

### Gas Phase

- ❖ Chemical vapor deposition
- ❖ Laser chemical vapor deposition
- ❖ Photochemical vapor deposition
- ❖ Plasma-enhanced chemical vapor deposition
- ❖ Metal organochemical vapor deposition

### Liquid Phase

- ❖ **Electrodeposition**
- ❖ Chemical bath deposition
- ❖ Successive ionic layer adsorption and reaction (SILAR)
- ❖ Anodization
- ❖ Electroless deposition
- ❖ Spray pyrolysis
- ❖ Liquid phase epitaxy
- ❖ Sol gel process



### 1.3 Electrodeposition Technique:-

This technique is also called as Electroplating technique. Electrodeposition is a versatile and valuable application that was invented. This technique is popular due to its inexpensive and simple process of fabrication of metallic coating. A very thin coating (less than a nanometer) can be done by this method to produce two-way mirrors. [1,2] Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction [3]. The semiconducting properties like n-type or p-type conductivity, variation in band gap like these properties can be easily controlled with equal accuracy. Nowadays materials like metals, semiconductors, ceramics, supercapacitors, conducting polymers, etc. are prepared by the electrodeposition technique. In industrial purposes, electroplating is used for making jewellery, paint on the body of cars or bikes, etc.

Preparation of thin films using the electrodeposition technique has several attractive features.

1. It is an isothermal process in which temperature remains constant. Morphology and thickness of the thin films can be easily controlled by parameters such as potential and current.
2. Structurally and compositionally modulated alloys and compounds can be deposited which are not possible with other deposition techniques.
3. Deposition on complex shapes is possible.
4. Relatively uniform films can be obtained on substrates.
5. The deposition rate is higher than all other physical and chemical methods.
6. The equipments required are cheaper and do not require sophisticated.
7. Toxic gaseous precursors need not to be used.
8. Does not require vacuum.
9. Generally operates on low temperature.



## 1.4 References

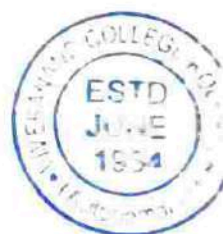
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**CHAPTER 2**  
**THEROTICAL BACKGROUND**

<b>Sr. No</b>	<b>Content</b>	<b>Page No</b>
2.1	Introduction	15
2.2	Different modes of Electrodeposition Method	22
2.3	Effect of Preparative parameters	24
2.4	References	28



## 2.1 Basics of Electrodeposition

The simple electroplating bath consist of an electrolyte contain metal ions, an electrode or substrate on which deposition is carried out and the counter electrode which is generally a platinum or graphite rod. When current is passed through electrolyte the cations and anions move towards the cathode and anode resp. and deposited on electrode after undergoing charge transfer reaction. Electrodeposition is based on principal of electrolysis in which it is due to passage of electric current through an electrolyte, chemical reaction occur at electrode electrolyte interface.

### Experimental setup of simple Electrodeposition technique

The substrate or object is that is to be plated is deep into the electrolyte i.e. electroplating bath which act as a negatively charged cathode. The positive charge is to be connected to the anode which is Graphite rod. A power source in the form of a battery provides the necessary current. This type of arrangement directs electrons into a path from the power supply to the cathod The schematic diagram explains the electrodepostion is shown in Fig.1.1

The typical electrodeposition set up consists of following components

1. Electrolyte
2. Electrodes (cathode and anode)
3. Source of electricity

#### 1. Electrolyte :-

A electrolyte bath contains chemical compound i.e. solution. This is conducting medium in which the flow of electric current take places by migration of ions. The bath may be contains aqueous, non aqueous or molten and it must be contain suitable metal salts. Very often the so formed solution itself is simple called and "Electrolyte" also molten salts and solution are often called "electrolyte"

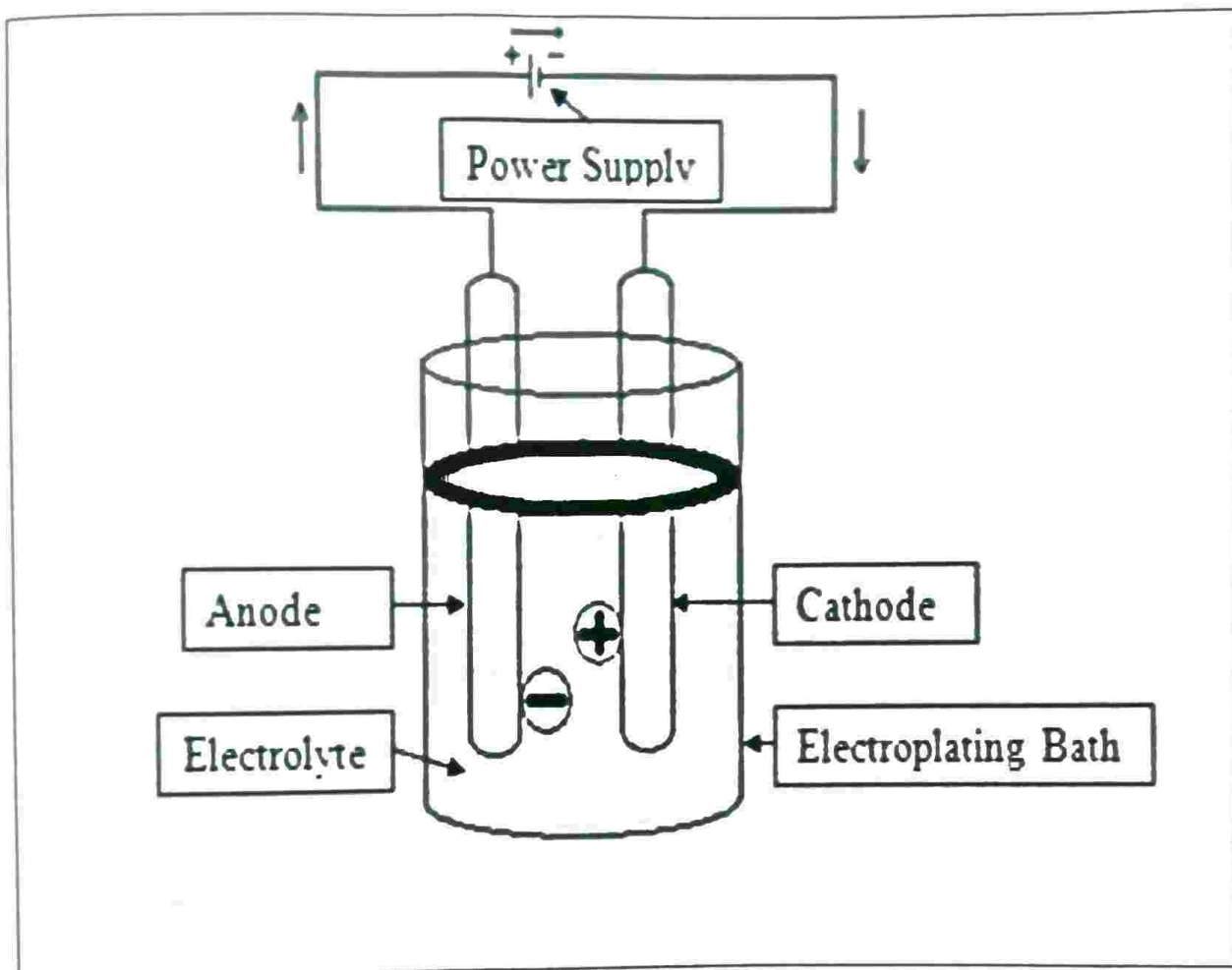
#### 2. Electrode :-

It is conductor through which an electric current passes. At least two electrodes are required. In that two electrodes is act as Anode and another is Cathode. These can be simple metallic structures like rod, sheets, etc. A negative terminal which is connected to cathode and positive terminal connected to the anode. At cathode positive ions are discharged or negative ions are formed. At anode negative ions are discharged or positive ions are formed.



### 3. Source of Electricity:-

A source of electrical power (electrical supply) is device that supplies electrical current. In this method DC supply were used. It can be electrochemical (Fuel cell or battery) or electromechanical device (dynamo) or specific instrument is called 'power supply (source)' or voltage source (supply) or current source (supply). With the DC supply at constant voltage the deposition technique known as Potentiostatic Deposition, DC supply at constant current known as Galvanostatic deposition & Current or Voltage are in pulses or in waveform is known as Potentiodynamic deposition



**Fig. Experimental setup of a simple electrodeposition technique**

- i. Standard electrode potential - A standard electrode potential is one of the equilibrium potential, for an electrode in contact with an electrolyte, in which all the components of a specified electrochemical reaction are in their standard state. The standard state for a gas at one atmospheric pressure, and it is constant for a solid.



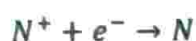
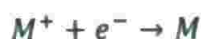


- ii. Reference electrode- A reference electrode which is used for the equilibrium the state of a given electrochemical reaction. It is permanently secured under constant physical and chemical condition. The passing of an electric current two electrodes are deeped in an electrolyte the potential is applied across them. The electric current through the electrolyte is due to cations and anions (+ve & -ve charged ions).

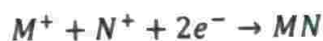
The net result is that metal (cation) is deposited on the cathode from the solution of metal ions according to following process. on the application of electric field  $M^{Z+}$  ions move towards the cathode and the elemental electrodeposition process can be written as



On the other hand, if the electrolyte contains more than one ionic species then it can be simultaneously deposited as,



Or



When a electrolysis is carried out in the electrolyte, metal is deposited on cathode at the same time anode is dissolved in the solution. The amount of dissolution and deposition is determined by the quantity of electricity passed. one can deposit a compound or an alloy of a multi component system. When an electrolysis (chemical changes due to electricity) is carried out in the electrolyte, metal is deposited on cathode at the same time anode (metal) is dissolved in the solution. The amount of dissolution and deposition is determined by the quantity of electricity passed.



## Faraday's Law of Electrodeposition:-

### Faraday's First Law

" The amount of substance liberated or deposited on the electrode is proportional to quantity of electricity passed. Mathematically  $W \propto Q$  where  $W$  is the amount of substance liberated in grams, and  $Q$  is the quantity of electricity passed through electrolyte in coulombs. If current  $I$  is passed for time  $t$  sec. then the quantity of electricity.

$$Q = I \times t$$

$$W \propto Q$$

$$W \propto It$$

$$W = z It$$

Here  $z$  is the proportionality constant i.e known as 'Electrochemical equivalent'

### Electrochemical equivalent:-

It is the amount of substance liberated or deposited in gram. When 1 ampere current is passed through electrolyte for 1 sec..or passing 1 coulomb electricity.

### Faraday's second law:-

"If the same quantity of electricity is passed through different electrolyte then the amount of substance liberated on the respective electrodes will be in the ratio their equivalent weights." Mathematically this statement relate the mass  $\Delta m$  deposited over a unit area to the current density  $j$  flowing for a time  $t$

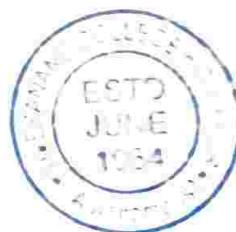
$$\Delta m = \text{const} \times jt$$

$$\Delta m = C_e jt$$

Where,  $\Delta m =$  mass liberated per unit area

$j =$  current density

$t =$  time



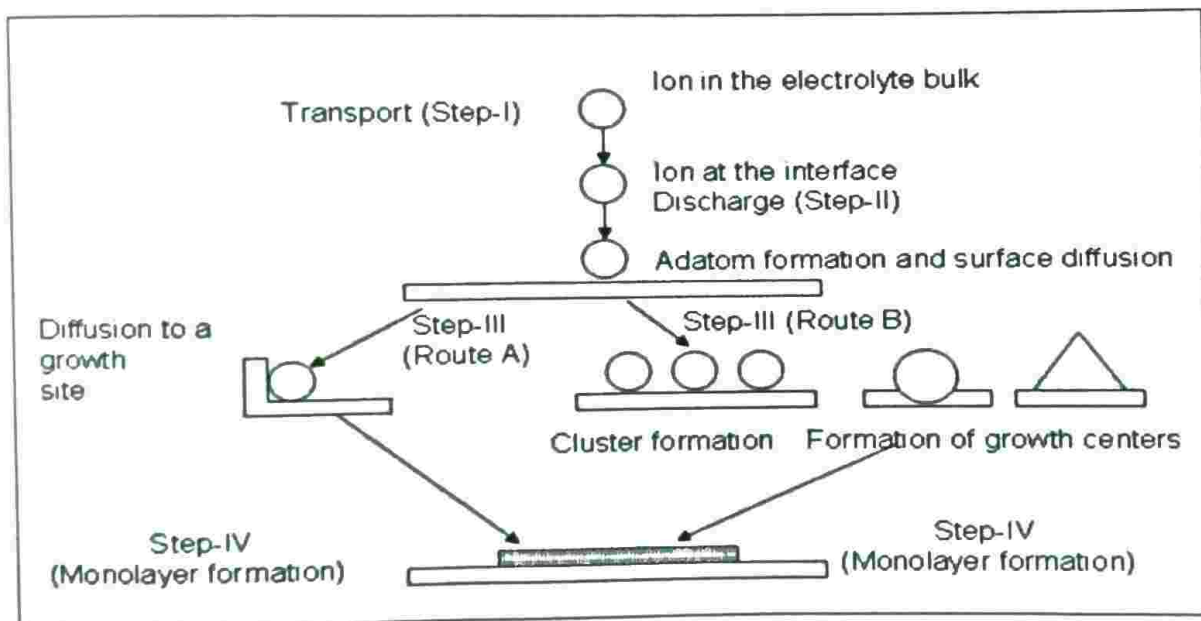
The rate of growth of electro deposit per unit area can be written as

$$\frac{d}{dt} \Delta m = C_e j$$

If  $z$  is the ionic charge, then  $j/zF$  gives the growth rate of the electrodeposition in gram molecules of the substance.

Steps involved in electrodeposition process

- i. Transport of the ions in the electrolyte towards the interface.
- ii. Discharge of the ions reaching the electrode surface.
- iii. Breaking of ion-ligand bond (when the bath is complex).
- iv. Incorporation of adatoms on the substrates followed by nucleation and growth. Two route are possible
- v. Formation of monolayer on the substrate.



**Fig 1.2: Schematic representation of steps involved in the electrodeposition process.**

All above steps occur within  $1-1000\text{\AA}$  from the substrate; however each has its own region of operation. These various processes can be classified with respect to distance from the electrolyte as:





a. In the electrolyte

b. Near the electrode

c. At the electrode

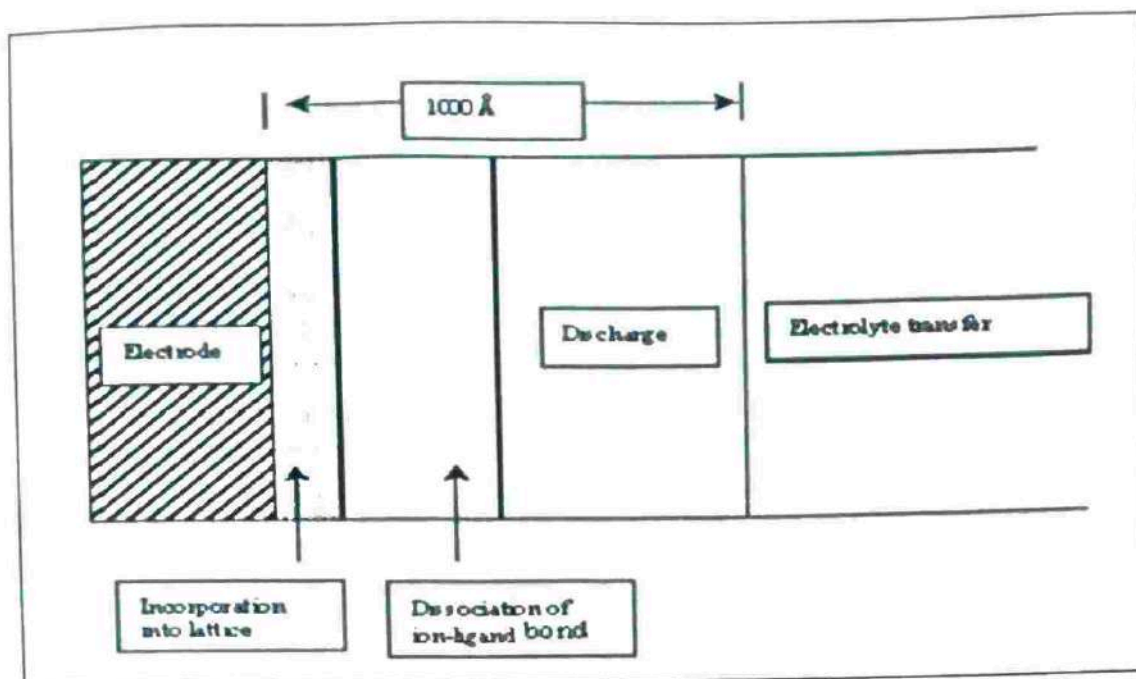


Fig 1.2 a Approximate regions in which various stages of ion transport occur leading to electrodeposition.

a. Process in the electrolyte:

The ions in the electrolyte can move towards the electrode under the influence of

1. Potential gradient leading to ion drift,  $df/dx$
2. Concentration gradient leading to diffusion of ions,  $dc/dx$
3. A density convective current,  $dr/dx$  due to consumption of ions at the electrode.

The general mathematical equation including all these processes can be written as

Nernst-Planck equation,

$$j = zF \left( \frac{Dc}{RT} \frac{d\phi}{dx} + \frac{dc}{dx} + cv \right)$$

Where,  $F$  is the Faraday's constant,  $v$  is the viscosity of the electrolyte,  $R$  is the gas constant and  $D$  is the diffusion coefficient. The three terms in the parenthesis respectively describe the contributions of migration, diffusion and convection processes to the mass transport towards the electrode.

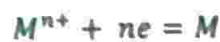


### b. Processes near the electrode but within electrolyte

Ionic species are normally surrounded by a hydration sheath or by other complex forming ion or ligand present in the electrolyte. They move together as a single entity and arrive near the electrode surface where the ion-ligand system either accepts electrons from the cathode (or donates electrons to the anode). This ionic discharge occurs between 10 to 1000 Å from the electrode.

The first case is similar to the homogeneous charge transfer reaction between two reacting species in solution. One can visualize two possible reactions for the case of charge transfer between the approaching  $M^{n+}$  ion and the electron of the metal

#### 1. Electronation reaction



#### 2. Deelectronation reaction



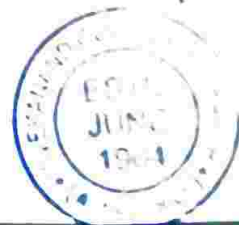
The net current density across interface is given by **Butler – Volmer** equation

$$j = j_0 \left[ \exp\left(-\frac{zF\alpha_c \eta_a}{RT}\right) - \exp\left(\frac{zF\alpha_a \eta_a}{RT}\right) \right]$$

Where,  $j_0$  = equilibrium exchange current,  $F$  = Faraday constant,  $\alpha_c$  = transfer coefficient of the electronation charge transfer reaction,  $\eta_a$  = activation overpotential,  $\alpha_a = 1 - \alpha_c$  (transfer coefficient for the anodic process).

### c. Processes that occur on the electrode surface

The discharged ions arrive near the electrode, where step by step they lead to the formation of a new solid phase or the growth of an electrodeposit. The atoms deposited have



a tendency to form either an ordered crystalline phase or a disordered amorphous phase. The electrodeposition formation steps of transport, discharge, nucleation, and growth are interlinked.

## 2.2 Different modes of Electrodeposition Method

Electrodeposition techniques can be classified according to the nature of the electric field applied across the electrolysis cell:

### 1. Potentiostatic mode :

In potentiostatic (i.e., constant dc potential) electrodeposition, different charge transfer reactions proceed under a steady-state condition at rates appropriate to the steady-state interfacial over potential and exchange current density. The choice of overpotential is dictated by the composition of the bath, the substrate, and the reversible potential of the species to be deposited. The standard electrode potentials serves as an approximate guide in finding the potential at which electrodeposition of a particular species will be possible, but in practice the actual deposition potential depends on number of factors such as the substrate-depositant interaction, the hydrogen over voltage, the interaction between the components during compound electrodeposition, and the polarization characteristics of the bath. Potentiostatic deposition is carried out under either pure activation, diffusion, or mixed control depending on the choice of the deposition potential. Important features of potentiostatic deposition are,

- i) It controls the potential of working electrode with respect to reference electrode.
- ii) The potential at counter electrode is driven to the required potential to establish the desired working electrode potential.
- iii) The output waveform gives the variation of cell current with time.





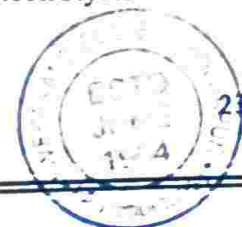
## 2. Galvanostatic mode :

With this mode, the deposition of elemental or binary(compound) semiconductor films can be obtained by keeping constant dc current between working and counter electrodes during deposition. For having uniform deposition it is necessary to have constant current density during deposition. Usually cathodic deposition (working electrode at negative potential) is preferred in this mode. The rate of deposition is proportional to the corresponding limiting current densities. The galvanostatic electrodeposition of compound semiconductor is complex as the codeposition depends upon optimum value of current density to be chosen correctly so that steady state overpotential satisfies thermodynamic conditions for codeposition. Important features of galvanostatic deposition are,

- i) It controls the current between counter electrode and working electrode at selected current range.
- ii) The counter electrode is driven to the potential required to establish the desired cell current.
- iii) Reference electrode is not used for controlling current but it is used to measure potential at some point in electrochemical cell.
- iv) The output waveform gives the variation of cell potential with time.

## 3. Potentiodynamic mode (Cyclic voltammetry):

This technique is used as an electrochemical analytical as well as varying potential electrodeposition technique. Potentiodynamic or cyclic voltammetry is a method in which electrolysis currents are measured as a function of imposed potential. This technique is a tool for studying the various electrochemical processes taking place during electrolysis such as



charge transfer, electrode kinetics etc. It gives qualitative information of electrochemical reaction. By studying cyclic voltammogram which is an electrochemical hysteresis redox potential of an electroactive species in the solution can be determined. In this technique, electrochemical process taking place entirely in the solution phase, a new solid phase is formed on the substrate surface due to the redox state. The solid phase must be formed by oxidation process. Metal oxides can be deposited in single step by using the potentiodynamic method. Film formation takes place by the reduction of metal ion (at reduction potential) on substrate followed by oxidation (at oxidation potential) of metal ions. Several repeated cycles can furnish a desired thickness of the film by following layer by layer deposition. These processes may in general written as,



In this solution  $X^-$  refers to the anion in the solution, Where 'Z' signifies total amount of product form after oxidation, '(1-Z)' signify the small amount of formed product reduced after deposition. Important features of potentiodynamic (cyclic voltammetry) deposition are,

- i) It measures the current during triangular potential sweep and observes both the anodic and cathodic responses.
- ii) The output waveform has both forward and reverse peaks that give information about the electroactivity of electrode or the solution.

### 2.3 Effect of preparative parameters:

The various preparative parameters like substrate, applied field and current density preparative parameters directly affect the structural, morphological and optical properties of bath temperature, complexing agents and pH of the bath etc. should be controlled to obtain



uniform, smooth and stoichiometric electrodeposits. Some preparative parameters are discussed below.

### **1. Substrate:**

Substrates play an important role in electrodeposition. Besides providing mechanical support to the electrodeposite, it influences on themorphological characteristics of the growing layer and on the electronic and optical properties of the electrodeposit. For the choice of suitable substrate following criteria should be applied for their selection.

- i. It should have good conductivity because it is one of the electrodes in electrodeposition. A good conductivity is beneficial in improving carrier collection efficiency.
- ii. The thermal expansion coefficient should match with that of electrodeposit. A mismatch may cause cracking or peeling of the film.
- iii. It should have good mechanical strength.
- iv. It should be stable in electrolyte bath.
- v. It should be smooth. Uneven, porous, voids and other irregularities influence the local current distribution. Metals have been widely used as substrates because of their good conductivity, easy availability, lower cost and relative ease of handling.

### **2. Bath temperature:**

The rise in bath temperature enhances the rate of diffusion and increases ionic mobility, hence the increase in conductivity of the bath. The increase in temperature increases the rate of crystalline growth favouring the coarse deposits. This increase in crystal size corresponds to decrease in polarization. At higher temperature, current densities increase, which increases the rate of nucleation, hence fine-grained, smooth deposits can be obtained. The rise in bath temperature decreases the hydrogen overvoltage so facilitates the evolution of gas, as well as precipitation of basic salts. The opposing effects make it difficult to predict





the choice of bath temperature; however, it can be optimized by performing actual experiments.

### 3. Current density :

At lower current densities (or over potentials) the discharge of ions occurs slowly, so the growth rate decreases but increases the crystallinity forming closely packed structures. As the current density is raised, the nuclei formation rate will increase and the deposit becomes fine grained. At higher current densities, the rate of discharge of ions becomes greater compared to rate of supply of ions and there is duplication of ions near the cathode, which favours the growth perpendicular to the substrate surface. Usually spongy, dendritic growth can be observed under this condition. Secondly, at very higher current densities, hydrogen evolution occurs at faster rate, which interferes the crystal growth and spongy, porous deposits may be obtained. This can also favour the precipitation of hydrous oxides or basic salts due to increase in local pH.

### 4. Metal ion concentration:

The plating bath is always an aqueous solution containing compound of metal to be deposited. It is always advantageous to use higher concentration of metal components in the bath solution. A high current density can be employed in high metal bearing bath. An increase in metal concentration, under given condition decreases the cathode polarization and increases the crystallite size.

### 5. Hydrogen ion concentration (pH):

In order to operate a bath with optimum efficiency and maintain the desired physical properties of the deposit, control of pH of plating bath is necessary. Besides too low pH may lead to accumulation of hydroxide ions in the vicinity of the cathode and consequent



precipitation of basic salts, which may get included in electrodeposition, thereby altering deposit properties. All aqueous solutions contain  $H^+$  ions; in fact in every deposit from an aqueous bath, there is a possibility of the hydrogen gas evolution at the cathode due to  $H^+$  ions. It takes place, the efficiency of metal deposition is lowered. As this efficiency and hydrogen discharge potential partly depends upon hydrogen ion concentration, at low pH, the bath permits the use of higher current density to produce a sound deposit with relatively high efficiency.

#### 6. Complexing agent:

The unstable metal ions are capable of combining chemically with neutral molecules and with ions of opposite sign to form stable complexion. The combination is through the covalent bond, when neutral molecules interact with positively charged metal ions to yield negatively charged complex ions. Complex compound in a plating bath serves two purposes. Firstly they make possible to maintain a high metal concentration but low metal ion concentration. The complex ions of the complex compound serve as a reservoir and continuously supply of the simple ions necessary for the discharge at the cathode occurs. A low metal ion concentration enables the production of deposits with small grains and improves the throwing power. Secondly, complex formation enables us to enhance appreciably the solubility of slightly soluble salts.



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# CHAPTER 3

## LITERATURE SURVEY

Sr. No.	Content	Page No.
3.1	Literature Survey	30
3.2	Reference	33



### 3.1 Literature survey of MnO<sub>2</sub> Thin film:

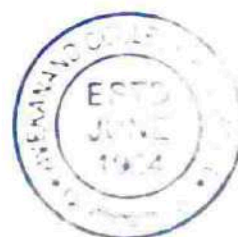
In recent years, manganese oxides have generated considerable scientific and technological interest because of their electronic and magnetic properties. There are four crystalline phases of manganese oxides (MnO, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, and Mn<sub>3</sub>O<sub>4</sub>) which have different structural and compositional properties and serve in various applications. Manganese dioxide (MnO<sub>2</sub>) can be used as a catalyst in oxidation–reduction reactions, as electrode materials in batteries, and in energy storage devices such as ultra capacitors. The dimanganese trioxide phase (Mn<sub>2</sub>O<sub>3</sub>) is quite attractive owing to its applications to produce soft magnetic materials to catalyze the removal carbon monoxide and nitrogen oxide from waste gas & in the catalytic combustion of methane. The hausmannite phase, Mn<sub>3</sub>O<sub>4</sub>, has also been shown to possess electro chromic properties. Furthermore, manganese oxide thin films serve as the substrate in the synthesis of magnetic oxide materials, which have important electrical and magnetic properties such as giant magneto resistance, and metal-insulator transitions. There are several oxidation states, including Mn(0), Mn(II), Mn(III), Mn(IV), Mn(V), Mn(VI), and Mn(VII) for manganese oxides.

Various methods have been reported for the preparation of manganese oxide materials to serve as electrodes for supercapacitors, such as the sol–gel technique, solution-based chemical routes, electrochemical deposition, hydrothermal method, electrostatic spray deposition (ESD) and sonochemistry. Most of these studies have focused on the synthesis methods with the goal of achieving enhanced electrochemical performance, e.g., a high specific capacitance, long-term cycling behaviour, and fast charging/discharging rate. Prasad and Miura prepared manganese oxide by potentiodynamic deposition on a stainless steel substrate and obtained specific capacitance of 480 F.g<sup>-1</sup> at scan rate of 10 mVs<sup>-1</sup>. Pang et al. prepared MnO<sub>2</sub> films by sol–gel synthesis with subsequent annealing at 573 K and reported the supercapacitance of 698 F.g<sup>-1</sup>. Toupin et al. reported manganese oxide synthesised by an easy method based on chemical reaction of potassium permanganate with manganese sulphate in aqueous solution. They reported specific capacitance of 180 F g<sup>-1</sup> from the untreated powder and, a little different value of 160 F.g<sup>-1</sup> from the powder heated for 3 h between 373 and 473 K, that was a 12% lower of the initial value. More recently, Brousse et



al. reported that long-term cycling behaviour with stable performance ( $>1, 00,000$ ) was realized in a carbon-MnO<sub>2</sub> hybrid electrochemical supercapacitor cells.

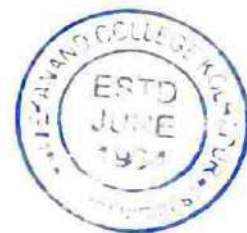
The literature survey shows that the MnO<sub>2</sub> and Fe: MnO<sub>2</sub> thin films have been prepared by physical as well as chemical methods. Physical methods are relatively expensive as compared to chemical methods. Our intention is to prepare MnO<sub>2</sub> and Fe: MnO<sub>2</sub> using simple and low cost electrochemical deposition method. It is one of the promising methods for the production of metal oxide films. This is probably the easiest, low cost, non-vacuum and suitable method to- prepare large area thin films, which has been also used for deposition of ferrite films.





### 3.2 Reference:-

- |  |
|--|
| [1] B. Cullity, "Elements of X-rays Diffraction", 2nd Edition, Addison-Wesley, London, (1978) 324-344                                  |
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## CHAPTER 4

### Synthesis and result

Sr. No.	Content	Page No.
4.1	Introduction	34
4.2	Deposition of thin films using ED method	34
	4.2.1 X-ray diffraction	34
	4.2.2 Substrate Cleaning	36
4.3	Preparation of solution	37
	4.3.1 Results and Discussion	40
4.4	Reference	44



## 4.1 Introduction

This chapter includes the growth of  $MnO_2$  thin films by electrodeposition method and investigation of structural, properties. The thin films of  $MnO_2$  were chemically deposited onto Steel substrate. The depositions were carried out by optimizing preparative conditions, such as bath temperature, pH, concentration and deposition time etc. to get uniform, adherent films

Structural properties of  $MnO_2$  thin films were studied by XRD pattern.

## XRD INFORMATION

### 4.2 Thin Film Characterization Method

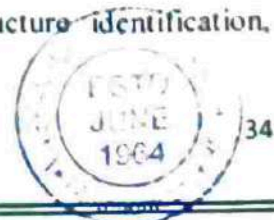
Summary of different characterization techniques used in the present study to find properties of the films

Sr. No.	Characterization techniques	Thin film properties
1	Cyclic voltammetry	For deposition potential
2	X-ray diffraction	Identification of material and crystallite size determination
3	Scanning electron microscopy (SEM)	Surface morphology
4	Raman Spectroscopy	Nature of Bonding
5	Optical absorption studies	Optical absorption coefficient and band gap

Different characterization techniques used for studying the properties of thin film materials. These techniques are as, cyclic voltammetry, X-ray diffraction (XRD), optical absorption techniques, scanning electron microscopy (SEM) and FT- Raman Spectroscopy.

### 4.2.1 Crystal structure Determination

X-ray diffraction (XRD) is a well-known technique to obtain the information of composition, phase and crystallite orientation of the material. Structure identification,





determination of lattice parameters and grain size are based on the X-ray diffraction pattern. Improved detection methods for X-ray, the availability of commercial monochromators and intense micro focus X-ray sources have made X-ray diffraction method applicable to films as thin as  $100\text{\AA}$ . The several workers have described x-ray diffraction arrangement, suited to the study of thin films. This technique employs a chromator to provide a diffracted beam, which is further diffracted from the film surface oscillating about the mean diffraction position. The x-ray diffraction technique based on monochromatic radiation is more important because the spacing of the planes (d-spacing) can be deduced from the observed diffraction angles. The phenomenon x-ray diffraction can be considered as reflection of x-rays from the crystallographic planes of the material and is governed by the Bragg's equation-

$$2d \sin\theta = n\lambda$$

Where 'd' is lattice spacing,  $\lambda$  is the wavelength of the monochromatic x-ray; 'n' is order of diffraction and  $\theta$  is diffraction angle. The 'd' values are calculated using above relation for known values of  $\theta$ ,  $\lambda$  and n. The X-ray diffraction data thus obtained is compared with American Standard for Testing for Materials (ASTM) to identify the unknown material.

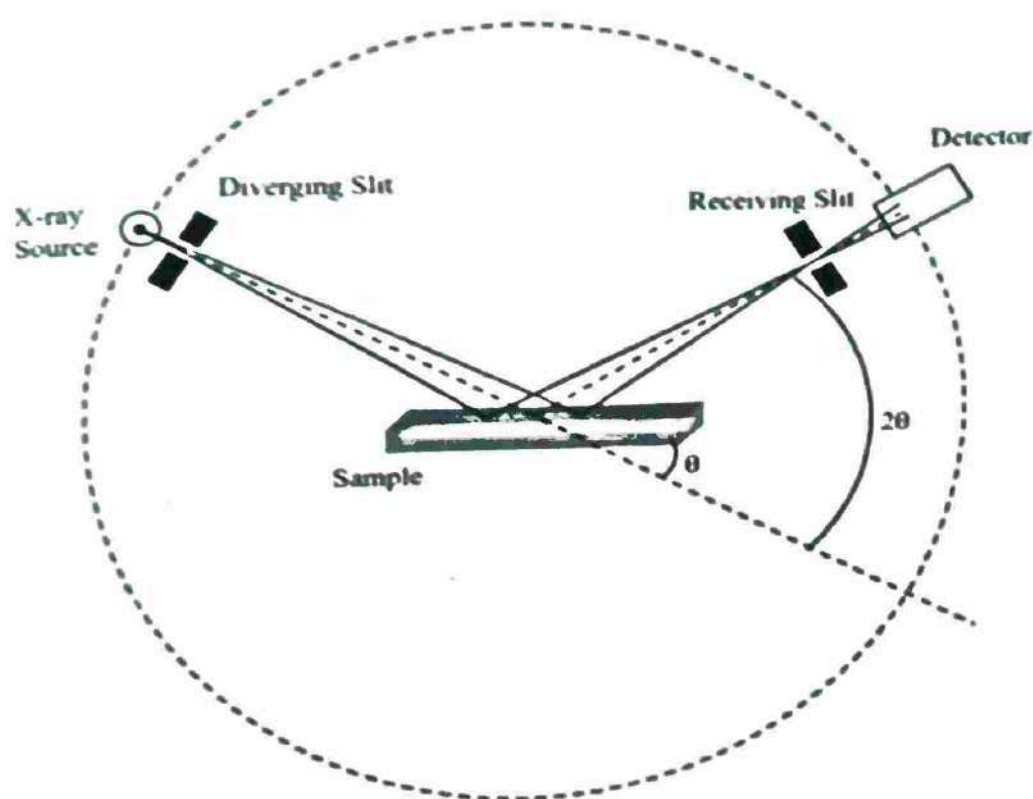
In powder diffraction method the crystal to be examined is reduced to a fine powder and placed in a beam of a monochromatic x-rays. Each particle of the powder is the tiny crystal, or assemblage of smaller crystals, oriented at random with respect to incident beam of x-rays. For example some of the crystals will be correctly oriented so that their planes, can reflect the incident beam. Other crystals will be correctly oriented for reflections and so on. The principle of x-ray powder diffractometer is that every set of lattice planes will be capable of reflection. Ideally, according to Bragg's law, for the particular d value, the constructive interference of x-rays should occur only at particular value i.e. Bragg's angle



and for all other angles there should be destructive interference and intensity of diffracted beam will be minimum for destructive interference.

#### Nature of Sample:

- 1) Powder
- 2) Single crystal and
- 3) Thin film



#### Uses/Advantages:

- 1) To determine a crystal structure and lattice parameters
- 2) To determine number of atoms per unit cell
- 3) To determine the density of material, particle size etc.
- 4) Less quantity of material is sufficient for characterization.

#### Limitations/Disadvantages:

- 1) For less material it is not possible to detect all characteristic planes



- 2) Cannot get any idea about surface morphology
- 3) One cannot study constituent multilayer individually

## Preparation of Solution

### 4.3 Deposition of $MnO_2$ thin films by electrodeposition

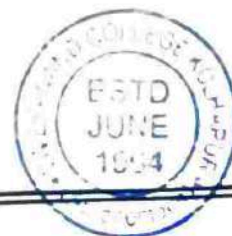
#### 4.3.1 Substrate Cleaning

Before any substrate can be used, it must be adequately cleaned. The proper cleaning technique depends on the nature of the substrate, the nature of the contaminants and the degree of cleanness required. Cleaning involves the breaking of adsorption bonds between the substrate and the contaminants without damaging the substrate surface itself. The following procedure has been adopted for cleaning of the Steel substrates:

1. Steel substrate was washed with double distilled water,
2. Polish with Zero number polish paper
3. Washed with double distilled water and
4. Ultrasonically cleaned with double distilled water for 10 min and used prior to the deposition.

#### 4.3.2 Preparation of solution:

The source of  $MnSO_4$  used was 0.02 M Several preparative parameters such as pH, concentration, current and time were optimized shown in table 3.2.2. The stainless steel were used as the substrates, which were cleaned with detergent and followed by rinsing with





double-distilled water and finally in the above bath and the bath was heated. when we applied potential, deposition of  $MnO_2$  took place on the substrate.

### Preparation of Solution

Solution concentration	$MnSO_4 + Na_2SO_4$
Ph	~2
Substrate	Stainless steel
Deposition current density	1.50 mA/cm <sup>2</sup>
Deposition temperature	Room temperature



### 4.3.3 X-Ray Diffraction (XRD) study

Fig.1. shows XRD patterns of Ni doped ZnSe thin film. It is observed that all films are polycrystalline in nature having hexagonal crystal structure, preferred orientated along (111) together with other planes (220) (400). Its  $2\theta$  are 28.45, 42.35, 69.50, respectively. Our results are in good agreement with the JCPDS Card No. 01-089-2940, which showed that Ni doped ZnSe thin film have hexagonal Structure. However, hexagonal wurtzite structure and cubic zinc blend structure, the lattice constants were evaluated using the relation,

$$d = \left[ \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \right]$$

Where,  $d$  is the inter-planar spacing of the atomic plane. The crystallite size  $D$  of the films was calculated from the Debye Scherer's formula from the FWHM.

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where,  $D$  is crystallite size and  $\beta$  is the FWHM.

The number of crystallites per unit area ( $N$ ) of the films was determined with the using formula,

$$N = \frac{t}{D^3}$$

Where,  $t$  is thickness of the film,  $N$  number of crystallites per unit area, and  $D$  crystallite size.

[2]

The texture coefficient was calculated using an expression,

$$p(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_o(h_i k_i l_i)} / \left[ \frac{1}{n} \sum \frac{I(h_i k_i l_i)}{I_o(h_i k_i l_i)} \right]$$

Where  $I_o$  represents the standard intensity,  $I$  is the observed intensity of  $(h, k, l)_i$  plane, and  $n$  is the reflection number [1,2].



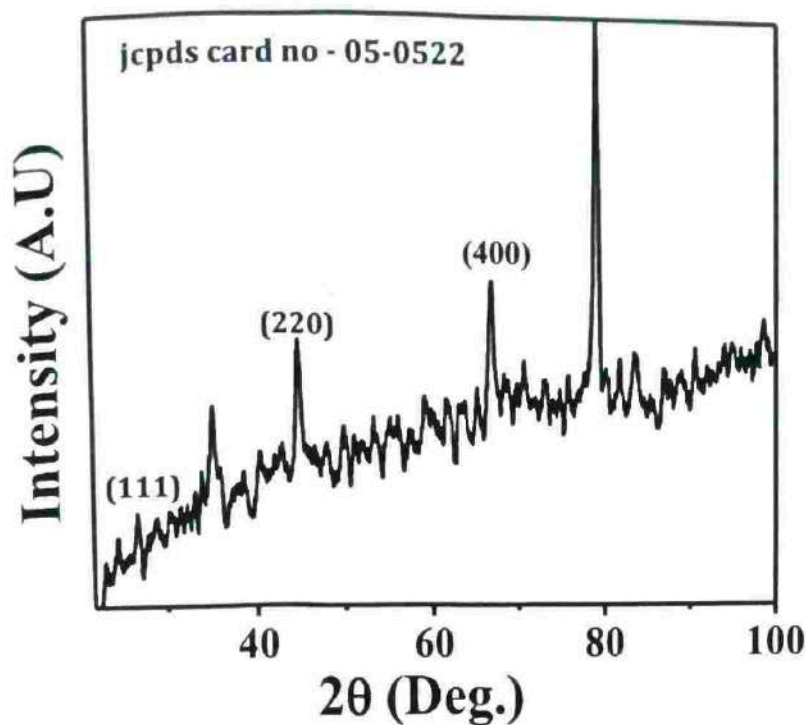


Figure 3.3.2: X-ray diffraction study of electrochemically synthesized pure MnO<sub>2</sub> thin films on stainless steel substrate.

The crystallite shape of the MnO<sub>2</sub> thin film is strongly related to the texture of MnO<sub>2</sub> film. The predominant plane orientation of the film has high texture coefficient value. The observed average crystallite size is 34 nm. The maximum texture coefficient is observed at 56.42°, means that orientation is along that direction. The number of crystal per unit area is  $N=1.07 \times 10^{16}$  per unit volume. The lattice constant is 5.86.

### 4.3 Results and Discussion

The electrochemically prepared pure MnO<sub>2</sub> thin films were characterized by different physico and chemical methods. The structural study was made with the help of X-ray diffraction (a Bruker D8-Focus diffractometer (XRD) operating with a Cu K $\alpha$  radiation source filtered with a graphite monochromator ( $\lambda=1.5406 \text{ \AA}$ ).





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# Chapter 5

## Summary and Conclusions



In the recent year, n-type materials in the form of thin film have received great attention by many scientists because of their interesting properties like transparent, conducting and wide band gap etc. In the field of material research, one is often confronted with problem of material preparation and in order to reduce cost, a relative simple method is needed to be able to assess quickly the various physical properties of material. Preparation of the materials in thin film is relatively easy and less expensive as compared that of growing in single crystal.

There are many methods of thin film preparation, such as chemical bath deposition (CBD), spray pyrolysis, electrodeposition, anodization, SILAR and so many high cost physical methods. Out of these methods electrochemical deposition method is relatively simple, low cost and can be used for preparation of large area thin film. It is found that no much work has been carried out  $\text{MnO}_2$  thin film by electrochemical method. In the present work,  $\text{MnO}_2$  films have been deposited using simple electrodeposition method and films are characterized for their structural, The work carried out is divided into four chapters.

In the chapter-1 the general introduction of the thin film and various deposition techniques are mentioned and general survey of  $\text{MnO}_2$  thin films is given. The purpose of project is stated there in.

The chapter -2 deals with theoretical background and basics of electrodeposition. Also the various thin film characterization techniques like crystal structure etc. are discussed in this chapter.

The next, chapter-3 describes details of preparation of  $\text{MnO}_2$  thin film using Electrodeposition method.

The chapter 4 deals with summary and conclusion of  $\text{MnO}_2$  thin films. The scan was initiated in from the potential 0.6V to -1.0 V Vs SCE, reduction wave's start at the -





0.17 V Vs SCE of the voltammogram. As the solution was added then there is shift in reduction potential was observed.

The XRD study was carried out for  $\text{MnO}_2$  thin film deposited on stainless steel substrate. The XRD pattern show  $\text{MnO}_2$  thin films are polycrystalline in nature with hexagonal crystal structure.

