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أ.د. نبيل علي بكر



*Republic of Iraq
Ministry of Higher Education &
Scientific Research
University of Diyala - College of Science
Department of Physics*



Structural and Optical Properties of Zinc Doped Nickel ferrite $\text{Ni}_{(1-x)}\text{Zn}_{(x)}\text{Fe}_2\text{O}_4$ Thin Films Prepared by Chemical Spray Pyrolysis Method

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By

Heyam Fadhil khudhair
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Supervised By

Prof. Nabeel Ali Bakr, (Ph.D.)

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(1-1) Introduction

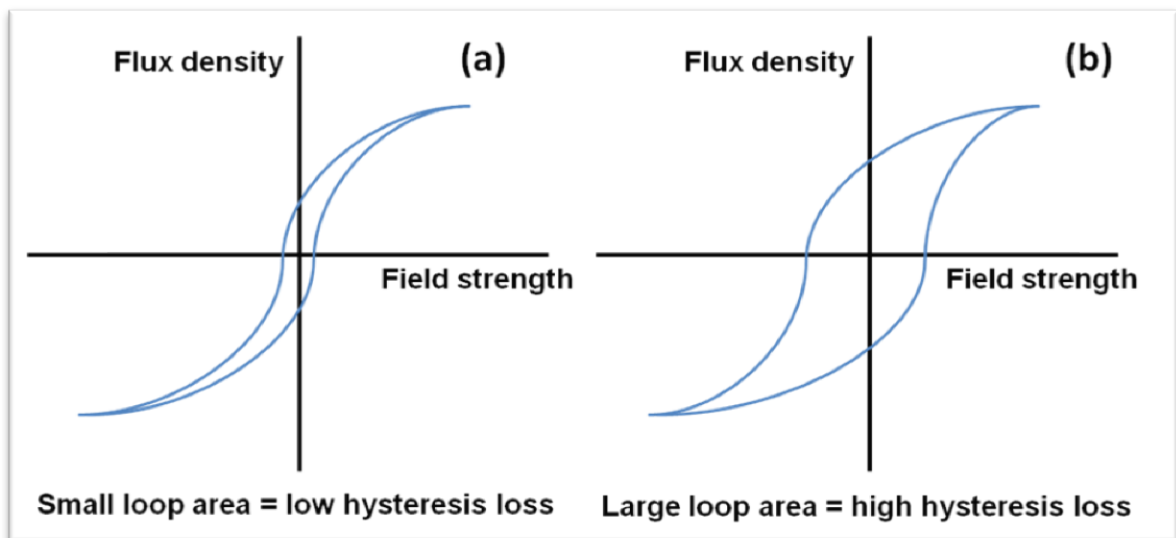
Ferrites are electrically ferrimagnetic ceramic compound materials, consisting of various mixtures of iron oxides such as Hematite (Fe_2O_3) or Magnetite (Fe_3O_4) and oxides of other metals like NiO, CuO, ZnO, MnO, CoO. The prime property of ferrites is that, in the magnetized state, all spin magnetic moments are not oriented in the same direction. Few of them are in the opposite direction. But as the spin magnetic moments are of two types with different values, the net magnetic moment will have some finite value [1].

The simplest among the ferrites are spinel type. Simple spinel ferrite has the general chemical formula ($\text{M}^{2+} \text{Fe}_2^{3+} \text{O}_4^{2-}$) or ($\text{MO} \cdot \text{Fe}_2\text{O}_3$), where (M) is a divalent metal ion and the crystal structure is that possessed by the mineral spinel. Mixed spinel ferrites have the general composition ($\text{M}_{1-x}^{2+} \text{B}_x^{3+} \text{Fe}_2^{3+} \text{O}_4^{2-}$). Mixed ferrites occur when the divalent metal (M) in the formula (MFe_2O_4) is a mixture of two divalent ions or (monovalent + trivalent) ions, while still retaining the spinel structure [2].

(1-2) Ferrite and Ferrite's Structure

Ferrites are chemical compounds with the formula of AB_2O_4 , where A and B represent various metal cations; usually including iron. Ferrites are considered a class of spinels that consist of cubic closed pack oxides with A cations occupying (1/8 th) of the octahedral voids and B cations occupying half of the octahedral voids. For the inverse spinel structure, half the B cations occupy tetrahedral sites and both the A and B cations occupy the octahedral sites.

Meanwhile, divalent, trivalent and quadrivalent cations can occupy the A and B sites and they include Mg, Zn, Fe, Mn, Al, Cr, Ti and Si. Ferrites are usually non-conductive ferromagnetic ceramic compounds derived from iron oxides as well as oxides of other metals. Like most other ceramics, ferrites are hard and brittle. Ferrites are widely used in high frequency applications because an AC field does not induce undesirable eddy currents in an insulating material. Based on the magnetic properties, ferrites are often classified as soft and hard ferrites as shown in Fig (1-1) [3].



Fig(1-1): Hysteresis loop for (a) soft and (b) hard ferrite [3].

(1-2-1) Soft Ferrites

Soft ferrites are characterized by a small value of coercivity so they cause low hysteresis loss at high frequency owing to which they are widely used in electromagnetic cores of transformers, switching circuits in computers and RF inductors; e.g., lithium ferrite, nickel ferrite and manganese-zinc ferrite [3].

(1-2-2) Hard Ferrites

Hard ferrites are characterized by a large value of retentivity and coercivity after magnetization so they find applications as permanent magnets in radios; e.g., barium and strontium ferrite. Maximum magnetic field strength is about (0.35 T) and magnetic field strength is about (30 to 160 kA/m). Ferrites are ferromagnetic materials that are typically oxides of mixed transition metals involving the iron. For example, MnFe_2O_4 and Mg-Zn ferrite are described as $\text{Mn}_{(1-x)}\text{Zn}_{(x)}\text{Fe}_2\text{O}_4$ [3].

(1-3) Types of Ferrites

Ferrites can be classified according to their structural into three different types [4].

- (1) Spinel ferrites (Cubic ferrites)
- (2) Hexagonal ferrites
- (3) Garnets

(1-3-1) Spinel Ferrites (Cubic ferrites)

Spinel is the most widely used family of ferrites. They are also called cubic ferrites. High values of electrical resistivity and low eddy current losses make them ideal for their use at microwave frequencies. The word spinel is derived from Italian *spinella*, diminutive of spine, thorn (from its sharply pointed crystals). Spinel crystallizes in the cubic system, forming octahedral crystals. There are at least (30) oxide minerals included in spinel super group. The majority of spinel compounds belong to the space group $\text{Fd}\bar{3}\text{m}$. The principal member of the group has the formula, AB_2O_4 ; the 'A' represents a divalent metal ion such as magnesium, iron, nickel, manganese and zinc. The quadrovalent lead ion can also occupy this site.

The 'B' represents trivalent metal ions such as aluminum, iron, chromium and/or manganese [4]. The chemical composition of a spinel ferrite can be written in general as MFe_2O_4 , where M represents a divalent metal ion with an ionic radius approximately between (0.6) and (1Å). In the case of simple ferrites, M is one of the transition elements Mn, Fe, Co, Ni, Cu and Zn, or Mg and Cd. A combination of these ions is also possible. The symbol M can represent a combination of ions which have an average valency of two e.g. Li^{1+} and Fe^{3+} in lithium ferrite, $Li_{0.5}Fe_{2.5}O_4$. The trivalent iron ions (Fe^{3+}) in $MeFe_2O_4$ can be completely or partly replaced by another trivalent ion such as Al^{3+} or Cr^{3+} , giving rise to mixed crystals with aluminates and chromites. The spinel lattice is composed of a close-packed oxygen arrangement in which (32) oxygen ions form the unit cell (the smallest repeating unit in the crystal network). These anions are packed in a face centered cubic (FCC) arrangement leaving two kinds of spaces between anions: tetrahedral coordinated sites (A), surrounded by four nearest oxygen atoms, and octahedral coordinated sites (B), surrounded by six nearest neighbor oxygen atoms. In total, there are (64) tetrahedral sites and (32) octahedral sites in unit cell, of which only (8) tetrahedral sites and (16) octahedral sites are occupied, resulting in a structure that is electrically neutral [5,6].

(1-3-2) Hexagonal

Hexagonal ferrites are widely used as permanent magnets and are characterized by possessing a high coercivity [4]. Hexagonal ferrites are classified into six main types depending on chemical formula and crystal structure. Their general formula is $MO \cdot 6Fe_2O_3$ where M can be Ba, Sr, or Pb. The most important of the hexagonal ferrites is barium ferrite, $BaO \cdot 6Fe_2O_3$. Barium ferrite crystallizes in the hexagonal magneto-

plumbite structure contains (10) oxygen layers in its elementary unit cell, and is constructed from four building blocks. Hexagonal ferrites are used widely as permanent magnets. The hexagonal ferrite lattice is similar to the spinel structure, with the oxygen ions closely packed, they are magnetically hard (unlike the cubic ferrites which are magnetically soft), Like the cubic ferrites, they are cheap to be produced by ceramic processing methods, and can be powdered and formed into any required shape.

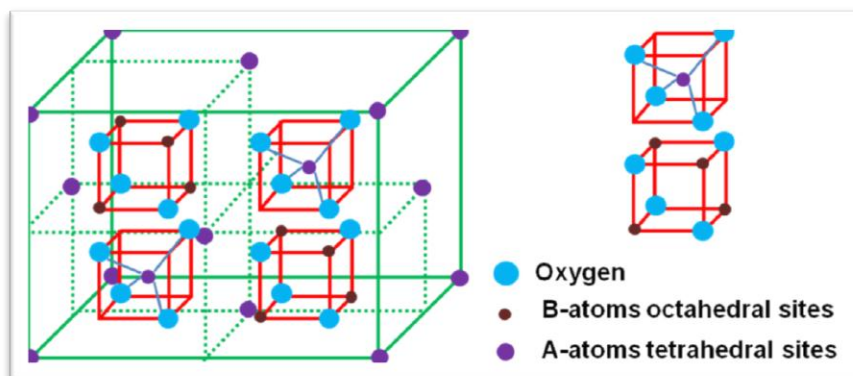
(1-3-3) Garnets

The garnets are rather weakly ferrimagnetic. As an example, in yttrium–iron garnet, the yttrium does not have a magnetic moment (since it does not have any f electrons), so the net moment is due entirely to the unequal distribution of Fe^{3+} ions in up- and down-spin sites. The garnets have the chemical formula $3\text{M}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$, where M is yttrium or one of the smaller rare earths, Since the rare earths readily substitute for one another, and Fe^{3+} can be easily replaced by Al^{3+} or Ga^{3+} , it is possible to tune the compensation point, saturation magnetization, anisotropy, and lattice constant for specific applications. Resistivity of garnets is extremely high, therefore they are used in very high frequency (microwave) applications, where even the ferrites would be too conductive.

(1-4) Unit cell structure of spinel ferrite

The unit cell of spinel ferrites consists of (32) oxygen, (16) trivalent iron, and (8) divalent metal ions. The most important feature of the unit cell is that its array of oxygen ions creates two kinds of interstices, which can be filled by the metal ions. These interstices are referred to as

tetrahedral or A sites and octahedral or B sites. Figure (1-2) shows the unit cell of spine structure. There are two groups of four cubes (octants). The ionic positions are different in two octants sharing a face or a corner and the same in two octants sharing an edge. Thus, to give a complete picture, it is necessary only to show the positions of the ions in two adjacent octants. Note that each octant contains a metal ion in the center (small violet sphere) surrounded by the tetrahedral of oxygen ions: this ion is said to occupy an A site. The right hand octant shows four metal ions (small red spheres) each surrounded by an octahedron (one of which is shown) formed by six oxygen ions. Such ions are said to occupy B sites. In a unit cell, there are (64) A sites, (8) of which are occupied, and (32) B sites, (16) of which are occupied. The divalent metal ions commonly used in ferrites can be classified into those preferring B sites (Co, Fe, and Ni) and those preferring A sites (Mn and Zn). In the normal spinel structure the (8) divalent metal ions go into the A sites and the (16) trivalent iron ions have preference for B sites. They will displace eight of the trivalent iron ions which go over into the A sites. This results in an inverted spinel. As two ionic species are then distributed over the octahedral sites, randomness may be present, contributing to the line width of the materials. These are, however, limiting cases [3].



Fig(1-2): The unit cell structure of spinel ferrite [3].

(1-5) Ferrite Thin Films

Thin films technology is one of the most accelerating fields in research. The film is said to be thin, if its thickness is less than (1 μm) [7]. Thin film plays an important role in many technological application including storage devices, microelectronics and surface coating etc. [8]. Thin films of magnetic materials can be a replacement of bulk material. These materials play a vital role in the development of advanced technology. These are being fabricated for the development of integrated circuit industry. In order to meet the demand for the progress of the miniaturization in electronic devices with more capacity and higher speed, it requires new techniques and new materials. Thin film cost is cheap compared to its corresponding bulk material [9].

(1-6) Applications of Ferrites Thin Film

Ferrites were first prepared by ceramic methods, involving milling, mixing, pressing, sintering, and finishing as basic operations, to obtain bulk materials with grains in the micrometric scale. However, as a result of the general current tendency to miniaturization and readily integrate ferrites into electronic devices, it is desirable to fabricate these ferrite materials in the form of thick and thin films and, more recently, nanostructured materials [10]. Ferrite thin films have recently received considerable attention on account of their potential industrial applications in high-density magnetic recording media, microwave devices, permanent magnets, magneto caloric refrigeration and the contrast agents for magnetic resonance imaging [11-13]. Soft magnetic thin films with high electrical resistivity are needed for developing micro inductors and micro transformers, monolithic microwave integrated circuits and humidity

sensor also [14]. In the case where ferrite materials are used for catalytic and magnetic or electrical applications, they are prepared in the form of ceramics materials with very high density. On the contrary, in applications for gas sensor devices, lower density and higher surface area are required [15]. In recent years, soft magnetic ferrite films with high resistivity and high complex permeability gained more interest in the field of high frequency applications such as RF broadband choke coils, planar inductors, EMI suppressors and magnetic sensors [16].

(1-7) Nickel-Ferrite Thin Films

Spinel ferrites with general formula AB_2O_4 are a large class of oxides with remarkable application possibilities from simple permanent magnets to microwave applications, magnetic recording, gas sensors, catalysts and photocatalysts. Generally, spinel ferrites have been applied for the last (70) years. From all ferrites the Ni–Zn spinel ferrites are important as microwave materials, due to its high resistivity and low coercivity. At the same time, Ni–Zn ferrites are structure sensitive and it is not easy to produce point-defect free, stoichiometric Ni–Zn ferrites for high resistivity applications.

Since the miniaturization tendency of the electronic components started in the (1990s), the spinel ferrites have been prepared in the form of nanostructured thick and thin films. Properties of ferrite films are depending on preparation route, due to its strong influence on type of the film (epitaxial or polycrystalline), microstructure, particle size, chemical homogeneity and cationic distribution between tetrahedral and octahedral sub-lattice sites.

Nickel ferrite a kind of soft magnetic materials is one of the most attracting class of materials due to its interesting and important properties and has many technical applications, such as in catalysis, sensors and soon [17].

(1-8) Mechanism of Thin Films Formation

Films growth may be divided into certain stages as shown in figure (1-3). These stages are as follows [18]:

1. Nucleation, during which small nuclei are formed that are statistically distributed (with some exceptions) over the substrate surface.
2. Growth of the nuclei and formation of larger islands, which often have the shape of small (crystallites).
3. Coalescence of the islands (crystallites) and formation of a more or less connected network containing empty channels.
4. Filling of the channels.

It is important to mention that after a certain concentration of nuclei is reached; additional particles do not form further nuclei but adhere to the existing ones or to the islands formed already.

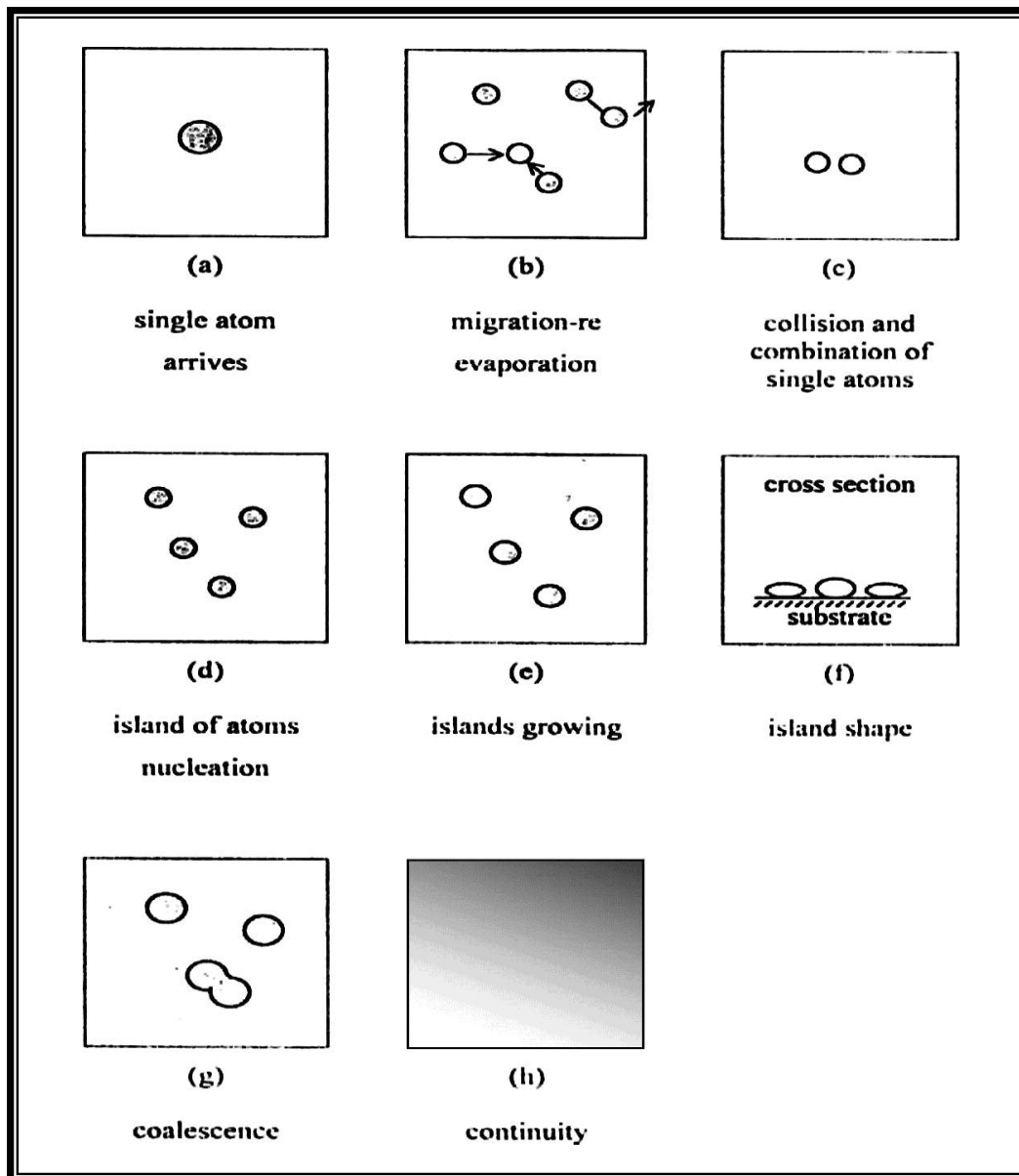


Fig. (1-3): Formation stages of thin film [19].

(1-9) Preparation Techniques of Ferrite Thin Films

The methods of preparing thin film can be divided essentially into two main groups namely physical and chemical methods [19]. In this study we used chemical spray pyrolysis method, These methods are shown in figure (1-4).

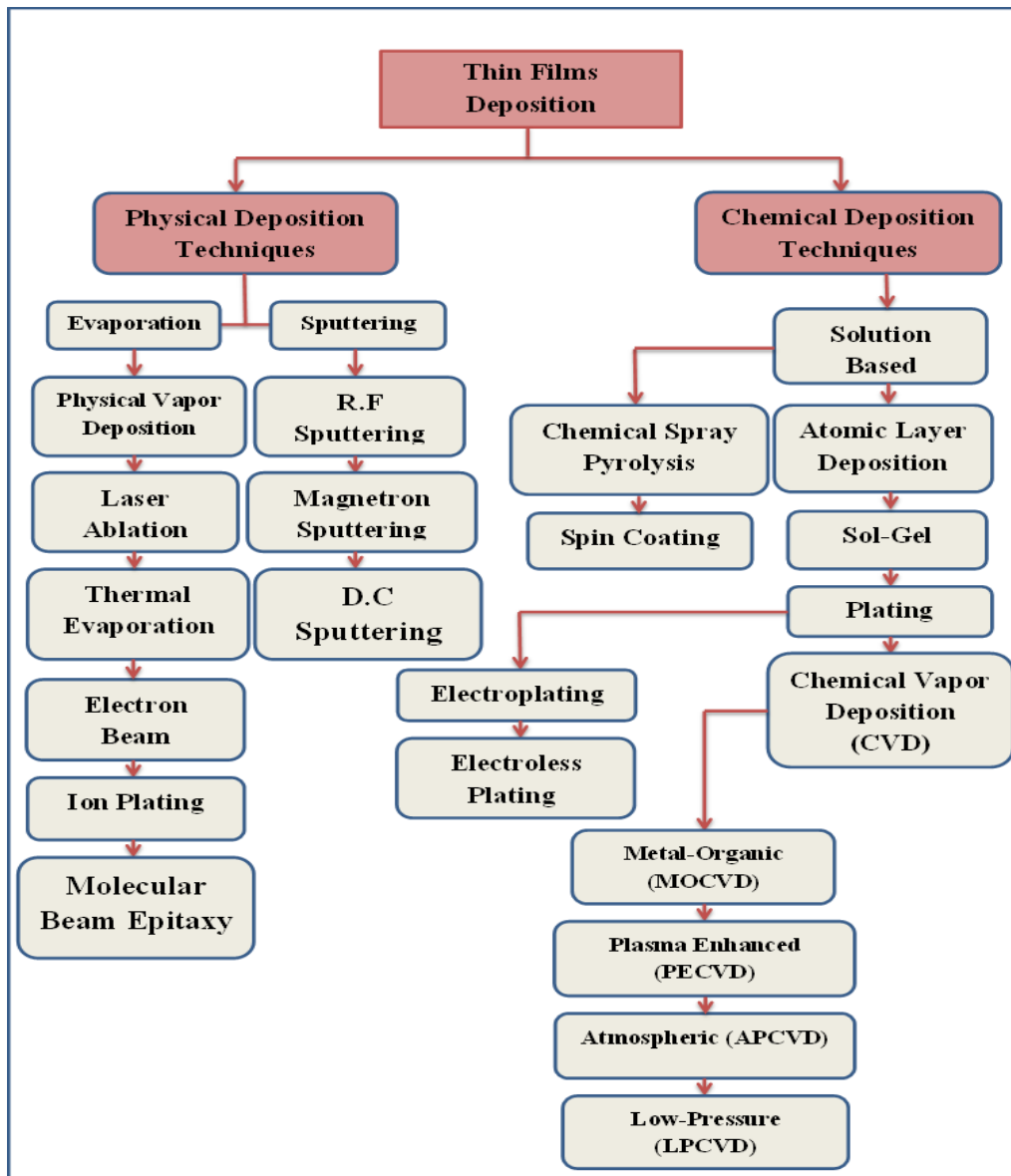


Fig. (1-4): Deposition Techniques of thin films [20].

(1-10) Literature Review

1- Lipare et al.(2003) [21] polycrystalline soft ferrites $Zn_xCu_{1-x}Fe_2O_4$ ($x = 0.30, 0.50, 0.70, 0.80$ and 0.90) doped with controlled amount of calcium chloride ($CaCl_2$) were prepared using standard ceramic route. The values of lattice constant increase as

doping percentage of CaCl_2 increased from (0.01%) to (0.05%) and after-wards decrease slightly. The variation of AC susceptibility with temperature shows the existence of single domain structure for ($x = 0.3$) and exhibits transition from single domain to multi-domain structure with increased Ca^{2+} contents from (0.01) to (0.1%). The composition ($x = 0.5$) shows multi-domain structure independent of Ca^{2+} content. The samples for ($x = 0.70, 0.80$ and 0.90) show paramagnetic behavior at and above room temperature.

- 2- **Takayama et al. (2004) [22]** studied the spray pyrolysis deposition of NiZn ferrite thin films. They investigated for the preparation of NiZn ferrite thin films from Ni, Zn and Fe nitrates mixed aqueous solutions at a substrate temperature between (350 and 500 °C) by a spray pyrolysis deposition (SPD). The crystallinity of the prepared NiZn ferrite films with the thickness of about (1 μm) became higher with increasing substrate temperature during a film deposition, but these as-prepared films could not show sufficient magnetic properties for practical use. Post-preparation annealing above (600 °C) was necessary to get enough magnetic properties. The NiZn ferrite film having the saturation magnetization of (0.37 T) was obtained after annealing at (750 °C) for (2 h) in air and the value was very close to that of the bulk ferrite. Also, it is noted that the film exhibited very high magnetic resonance frequency exceeding the value from Snoek's limit for a bulk specimen.
- 3- **Sorescu et al. (2005) [23]** studied the structural and magnetic properties of NiZn and Zn ferrite thin films obtained by laser ablation deposition. Laser ablation deposition had been used to synthesize nanoscale ferrite structures. The investigations were performed on NiZn and Zn ferrite films deposited on silicon (100) substrates. Films

produced by laser ablation at room temperature were annealed at (550 °C) for (1h). Other films were deposited directly at a (550°C) substrate temperature without subsequent annealing. Complementary x-ray diffraction and superconducting quantum interference device magnetometry measurements helped to identify the optimum laser ablation deposition conditions for obtaining the desired nanoferrite structures. From the hysteresis loops at (300 and 10K). They identified the paramagnetic or ferromagnetic behavior of the films.

- 4- **Tehrani et al. (In 2009) [24]** studied Ferrite nanocrystals Which are interesting material due to their rich physical properties. Here they add nonmagnetic dopants Zn and Cu to nickel ferrite nanocrystals, $\text{Ni}_{(1-x)}\text{M}_{(x)}\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$, $\text{M} \in \{\text{Cu}, \text{Zn}\}$), and characterize how relevant properties of the samples are modified accordingly. Basically, these dopings cause a rearrangement of Fe^{+3} ions into the two preexisting octahedral and tetrahedral sites. In fact, this, they show, induces pertinent magnetic properties of the doped samples. In the case of the Cu-doping, the Jahn-Teller effect also emerges, which they identify through the FTIR Spectroscopy of the samples. Moreover, they show an increase in the lattice parameters of the doped samples, as well a superparamagnetic behavior for the doped samples is shown, while the Jahn-Teller effect precludes a similar behavior in the CuFe_2O_4 nanocrystals. The influences of Zn and Cu substitutions are investigated on the optical properties of nickel ferrite nanocrystals by photoluminescence measurement at room temperature.

5- **Chavan et al. (2010) [25]** studied the structural and optical properties of nanocrystalline Ni–Zn ferrite thin films. Nanocrystalline ferrite thin films of $\text{Ni}_{(1-x)}\text{Zn}_{(x)}\text{Fe}_2\text{O}_4$ (with $x = 0.0\text{--}1.0$, in the steps of $x = 0.2$) were prepared successfully by chemical bath deposition (CBD) method using nickel (II) chloride, zinc (II) chloride and iron (II) chloride as a constituent materials. The prepared thin films were characterized by X-ray diffraction (XRD) technique, scanning electron microscopy (SEM), infrared spectroscopy (IR) and UV–vis spectrophotometer at room temperature. X-ray diffraction studies revealed the formation of single phase spinel structure of the film. The crystallite size was determined using Scherrer formula and it was found to be of the order of (16–20 nm). The band gap value varies from (1.55 eV) to (1.66 eV) for varying zinc composition. The experimental results show that, CBD method allows the synthesis of nanocrystalline $\text{Ni}_{(1-x)}\text{Zn}_{(x)}\text{Fe}_2\text{O}_4$ films with cubic spinel phase.

6- **Pawara et al. (2011) [26]** studied Synthesis of nanocrystalline nickel-zinc ferrite ($\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$) thin films by chemical bath deposition method, The nickel-zinc ferrite ($\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$) thin films had been successfully deposited on stainless steel substrates using a chemical bath deposition method from alkaline bath. The films were characterized by spectra showed strong absorption peaks around (600cm^{-1}) which are typical for cubic spinel crystal structure. SEM study revealed compact flakes like morphology having thickness ($\sim 1.8\mu\text{m}$) after air annealing. The annealed films were super hydrophilic in nature having a static water contact angle (θ) of (5°C).The electrochemical supercapacitor study of $\text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$

thin films had been carried out in (6M KOH) electrolyte. The values of interfacial and specific capacitances obtained were (0.0285 Fcm^{-2}) and (19 Fg^{-1}), respectively.

7- **Sutka et al. (2012) [27]** studied the properties of nanocrystalline, homogeneous spinel $\text{Ni}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ thin films deposited on glass substrates by using spray pyrolysis of metal nitrate aqueous solutions. The thickness of deposited films was below (500 nm), but crystallite size was under (30 nm). It had been shown that the DC resistivity, dielectric loss and optical band gap of deposited films were influenced by the zinc content. High DC resistivity and low dielectric losses of thin $\text{Ni}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ films were explained by mixed n-p conductivity and nanograin structure of spray pyrolysis deposited coatings which were changing with the ratio of Ni/Zn.

8- **Sutka et al. (2013) [28]** studied the electric and dielectric properties of nanostructured stoichiometric and excess-iron Ni–Zn ferrites in this paper, they report a study of the effect of excess iron on structural, microstructural, electric and dielectric properties of the nanostructured Ni–Zn ferrites $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_{2+z}\text{O}_{4-\delta}$ of different compositions with $x = 0, 0.3, 0.5, 0.7, 1$ and $z = 0, 0.1$. The structural and microstructural properties are estimated from x-ray diffraction and atomic force microscopy (AFM) data. The average grain size, evaluated from AFM topographical analysis, is found to be below (70 nm). The samples exhibit low values of dielectric constant and dielectric loss and a high resistivity. Contrary to earlier conclusions regarding micro structured Ni–Zn ferrites, in nanostructured Ni–Zn ferrites sintered at relatively low temperature and duration, the excess

of iron in the composition increases the electrical resistivity and reduces the dielectric constant and loss tangent.

- 9- **Kumbhar et al. (2014) [29]** studied the synthesis and characterization of Spray Deposited Nickel-Zinc Ferrite thin films, Thin films of nickel-zinc ferrite with general formula $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ (where $x = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$) had been prepared using spray pyrolysis technique onto the glass substrates at optimized substrate temperature of ($400\text{ }^\circ\text{C}$). The nickel nitrate, zinc acetate and ferric nitrate were used as precursor materials with double distilled water as solvent. As deposited films were annealed at ($600\text{ }^\circ\text{C}$) for (2 h). The X-ray diffraction (XRD) analysis reveals that the $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ thin films were polycrystalline with spinel cubic structure.
- 10- **Raghavender et al. (2015) [30]** studied the effect of zinc doping on the structural and magnetic properties of nickel ferrite thin films fabricated by pulsed laser deposition technique. Zinc, as known as non-magnetic element, had been doped into nickel ferrite under thin film form to modify its structural and magnetic properties. Laser ablated $\text{Ni}_{(1-x)}\text{Zn}_{(x)}\text{Fe}_2\text{O}_4(0.0 \leq x \leq 0.5)$ thin films grown on R-cut Al_2O_3 (0001) substrates using pulsed laser deposition (PLD) technique were single phase with (111) orientation, and they were strongly room temperature ferromagnetic. Compared to other Ni–Zn ferrite thin films they observed the enhancement in coercivity H_c .

(1-11) Aims of the Present Work

The main objectives of this work are:

- 1- Preparation of $\text{Ni}_{(1-x)}\text{Zn}_{(x)}\text{Fe}_2\text{O}_4$ thin films where $x = (0, 2, 4, 6, 8, \text{ and } 10\%)$ on glass substrates by spray pyrolysis (CSP) technique at substrate temperature of $(400 \pm 10 \text{ }^\circ\text{C})$.
- 2- Studying the effect of Zinc concentration on surface morphology, structural and optical properties of the deposited thin films.