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Synthesis $CoLa_xFe_{2-x}O_4$ As Anano Composite by SoL-GeL Technique.

A Thesis

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تحضير $(CoLa_xFe_{2-x}O_4)$ كمتراكب نانوي بطريقة المحلول الغروي الهلامي

رسالة
مقدمة إلى قسم الفيزياء - كلية العلوم – جامعة ديالى
وهي جزء من متطلبات نيل درجة الماجستير في علوم الفيزياء

من قبل
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Chapter One

1.1 Introduction

The history of magnetic materials apparently to go with the development of human civilization. Chinese are understood to have used the compass even before (2500) B.C. The Greek literature from (600) B.C. mentioned the power of magnets to attract iron. The scientific story of magnetism begun with a mineral called magnetite (Fe_3O_4). The word Magnet is derived from then Greek word 'Magnesia' in old English it was used for finding direction and was called 'Lode stone, meaning 'way stone. Magnetism is more of an experimental one than the others in the area of physics. In the sense that other experimental knowledge for superiority the theoretical understanding of the fundamental properties of matter [1]. To mention one example, how a high quality magnetic recording tape of disk does work it is not much understood but these media are made by trial and error method. Now Magnetism has become a popular subject [2]. In (1909) the German Scientist Hilbert first, his thought of the possibility of collection high electrical resistivity of the oxides with magnetic properties wanted in terms of magnetic material be appropriate practice for high frequencies were the result of research in this direction discovery of ferrite [3]. Ferrites with spinel structure represent the important class of magnetic materials consisting of ferric oxide and metal oxides. The spinel ferrites are widely studied result of their numerous applications in several fields, the spinel ferrite is having the chemical formula MFe_2O_4 where M is a divalent metal ions such as Co, Ni, Mn etc. While still maintain the spine structure [4]. Ferrites are ceramic, homogeneous materials composed of various oxides with iron oxide as their main constituent. Depending on the magnetic properties, ferrites can be categorized as "soft" and "hard" ferrite. Soft

ferrites have low corecivity while the hard ferrites have high corecivity. Hard ferrite have high corecivity and moderate magnetization corecivity stands for the resistance to get demagnetized for removal of the applied field which satisfy it for being a permanent magnet [5].

1.2 Advantages of Ferrite [6].

1. Wide frequency range used (10 kHz to 50 MHz).
2. Low cost.
3. Large selection material.
4. Shape versatility.
5. Economical assembly.
6. Temperature and time stability.

1.3 The Spinel Structure

Spinel ferrites is the most widely used family of ferrites which are called cubic ferrites .The spinel structure is derived from the mineral spinel ($MgAl_2O_4$ or $MgO.Al_2O_3$) whose structure was elucidated by Bragg (1915) [7]. The chemical composition of a spinel ferrite can be written in general as MFe_2O_4 where M is a divalent metal ion such as (Co^{2+} , Mg^{2+} ,Cd^{2+}, Cu^{2+}) or a combination of these ions. The unit cell of spinel ferrite belongs to the cubic structure formed by(8) molecules and may thus be written as $M_8Fe_{16}O_{32}$ and consisting of (32) of O^{2-} anions .The oxygen anions form the close face-centered cube (Fcc) packing consisting in(64) tetrahedral (A) and (32) octahedral (B) empty spaces partly populated by Fe^{3+} and Me^{2+}cations [8]. Figure (1.1) shows the unit cell of spinel structure.

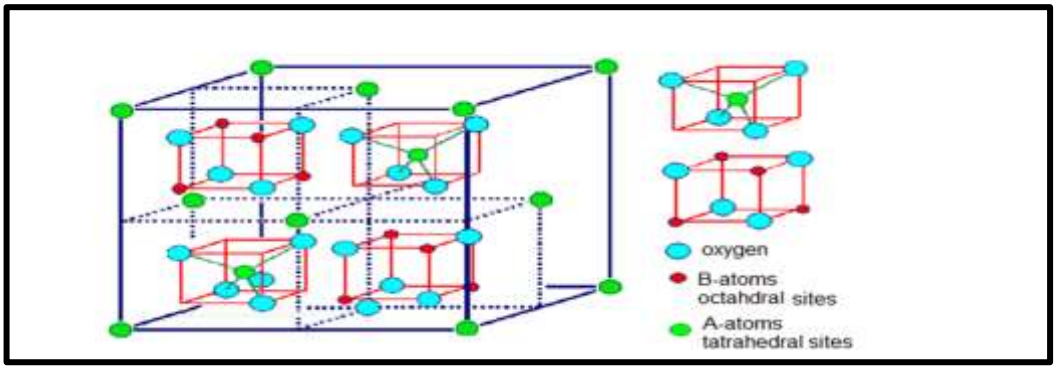

Figure (1.1) the geometry of the occupied interstitial sites in spinel structure.

1.4 Types of Spinel Ferrites

The oxygen ions in the spinel structure form an fcc lattice and the A^{2+} valence and B^{3+}valence ions occupy tetrahedral and octahedral interstitial sites, depending on the spinel type.

1. Normal spinel Structure

2. Inverse spinel Structure

1.4.1 Normal Spinel Structure

In the unit cell of spinel structure, there are (8) $MO.Fe_2O_3$ molecules. In this structure the eight M^{2+} ions occupy eight tetrahedral sites and the (16) Fe^{3+} ions occupy (16) octahedral sites [9]**.**

1.4.2 Inverse Spinel Structure

In the inverse spinel structure there are (8) M^{2+} ions that occupy (8) octahedral sites and the (16) Fe^{3+} ions are divided into (8) octahedral sites and (8) tetrahedral sites [9]**.** Table (1.1) show metal ion arrangements in spinel ferrite unit cell.

Table (1.1) Metal ion arrangements in spinel ferrite unit cell with composition ($MO.Fe_2O_3$) [9].

Types of interstitial site	Number available	Number occupied	Normal spinel	Inverse spinel
Octahedral	64	8	8 M^{2+}	8 Fe^{3+}
Tetrahedral	32	16	16 Fe^{3+}	8 Fe^{3+} 8 M^{2+}

1.5 Cobalt Ferrite

Cobalt ferrite is categorized into a hard magnet due to its high corecivity and moderate magnetization. Due to its high magnetic corecivity value and good physical and chemical stability it has been used for various applications. Cobalt ferrite $CoFe_2O_4$ neither has a spinel or invers spinel structure. It has partially inverse spinel structure.

$[Co_x^{2+}Fe_{1-x}^{3+}](Co_{1-x}^{2+}Fe_{1-x}^{3+})O_4$ having a coercivity value of 1000 Oe and moderate magnetization of 50 emu/g. Due to its high value, they become a perfect for using in high density magnetic storage materials, Ferro fluids, medical diagnosis, magneto-mechanical, and torque sensors [10].

1.6 Applications of Ferrites

Ferrites are very important magnetic materials because of their high electric resistivity they have wide applications in technology, particularly at high frequencies. Ferrites are used widely due to their following properties [11].

1. Ferrites are part of low power and high flux transformers which are used in television.
2. Soft ferrites were used manufacturing inductor core in combination with capacitor.

Circuits in telephone system, but now a days, solid state devices have replaced them. The soft Ni-Zn and MN-Zn ferrites are used for core manufacture.

3. Ferrites are used in microwave devices like circulators, isolators, switches Phase Shifters and in radar circuits.

4. Ferrites are used in high frequency transformer core and computer memory i.e. computer. Hard disk, floppy disks, credit cards, audio cassettes, video cassettes and recorder heads.

5. Ferrites used in magnetic tapes and disks are made of very small needle like particles of Fe_2O_3 or CrO_2 which are coated on polymeric disk. Each particle is a single domain of size (10-100) nm.

6. They are used as electromagnetic wave absorbers at low dielectric values.

1.7 Literature Survey

J. B. Silva et al. (2004) [12] clarified that Nano crystalline $CoFe_2O_4$ powders were synthesized using metallic nitrates dispersed in aqueous media precipitated by stoichiometric amount of NH_4OH. The influence of heat treatment on the texture and morphology of the cobalt ferrite powder was studied. The specific surface area varied from (150 to 1) m^2 /g while the average crystallite size varied from (17 to 100) nm with the annealing temperature.

A.T .Raghavender and K. M. Jadhav. (2009) [13] mentioned that a series of polycrystalline spinel ferrites with composition $CoFe_{2-x}Al_xO_4$ ferrites $(0 \leq x \leq 1)$ were prepared by the sol–gel method. The particle size (D) of all the samples decreases with increase in Al-content. The lattice constant and X-ray density decreased with increase in AL-content. The dielectric constant and loss decreases rapidly with increasing

frequency, and then reaches a constant value. Hence much lower dielectric constants obtained for the ferrites are used in the applications at high frequencies as microwave absorbers. The dielectric constant and loss tangent (tanδ) decreases with increasing with Al^{3+} ions substitution for the samples $CoFe_{2-x}Al_xO_4$ with $(0 \leq x \leq 1)$.

S. Singhal et al. (2010) [14] states .The zinc substituted cobalt ferrite nanoparticles ($Co_xZn_{1-x}Fe_2O_4$; with x = 0.0, 0.2, 0.4, 0.8 and 1.0) were prepared via sol-gel route. The particle sizes of the as obtained powders were found to be (~10 nm) which increases up to (~ 92 nm) on annealing at ($1000^{\circ}C$). The x-ray densities for all the annealed samples are increases linearly with increasing zinc concentration, which should be due to the heavier weight of zinc atom as compared to that of cobalt atom. The diffraction pattern did not show any peaks for the as prepared ferrite samples there- by showing the amorphous nature of the samples. However for the annealed samples regular peaks were observed, which confirmed that particle size increases with increase in temperature and the intensity of the peaks grew stronger with the grain size growth. It is observed that the lattice parameter increases linearly with increase in zinc concentration, the reason for this increase of lattice parameter values may be due to the larger ionic radii of Zn^{2+} as compared to Co^{3+}.

S. S. madani et al. (2012) [15] cobalt ferrite $CoFe_2O_4$ powders with Nano crystalline sizes were produced by a combination of sol-gel auto-combustion and ultrasonic irradiation methods employing a mixture of urea, thiourea and glycine as the fuel with the corresponding metal nitrates. The pH in the starting solution affects the combustion process, and then determines the particle size of the as synthesized powder. The influence of the pH value on the gel auto-combustion and the phase composition of the

synthesized powders have been studied with the help of scanning electron microscopy (SEM) observations, Fourier transform infrared (FTIR) spectroscopy and X-Ray diffraction (XRD) techniques. The synthesized powders had a particle size distribution in the range of (23-43) nm.

E. Pervaiza and I.H.Gula. (2012) [16] the gadolinium substituted Co-ferrites Nano crystalline $CoGd_xFe_{2-x}O_4$ (x =0.0 to 0.1) has been prepared by sol-gel auto combustion technique. Structural and morphology studies were performed using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Indexed XRD patterns confirm the formation of pure cubic spinel phase. Average crystallite sizes ranges from (16 nm to 25 nm ±2). Due Lattice constant (a) and crystallite size D (311) increases with increase in Gd^{3+} concentration to large ionic radii (0.94nm) of Gd^{3+} replacing Fe^{3+} (0.64nm). FT-IR analysis shows the presence of two expected bands attributed to tetrahedral and octahedral metal oxygen vibrations. SEM images show the spherical morphology and uniform size distribution. Room temperature DC electrical resistivity decreases ($\sim 10^6$) for (x=0.025) then increases up to(x=0.1 ~ 2.67×10^8) Ω-cm. Dielectric properties have been studied in the frequency range of (1 kHz to 5 MHz) Permittivity and tangent loss (tanδ) decreases with the substitution of Gd^{3+} in parent crystal structure and have values of (12.4) and (0.0160) at (5 MHz) respectively.

A.B. Shinde et al. (2013) [17] the indium substituted cobalt ferrite having general molecular formula $CoIn_xFe_{2-x}O_4$ (for x= 0.0, 0.3, 0.5) have been prepared by sol-gel auto combustion technique. The as prepared sample was sintered at 600 °C for 4hr. The X-ray diffraction pattern reveals the formation of single phase indium substituted cobalt ferrite samples. The

lattice constant obtained from (XRD) data increases with increase in indium substitution x. The Particle size obtained from XRD data is in the nanometer range. The particle size decreases with increase in indium substitution x. The average grain size obtained from Scanning electron microscopy technique is in nanometer range.

S. singhal et al. (2013) [18] in this work cadmium substituted cobalt ferrite non-collinear (spin canted) ferrites having the formula, $CoCd_xFe_{2-x}O_4$ (x = 0·0, 0·2, 0·4, 0·6, and 1·0), have been prepared by sol–gel auto combustion method. The ferrite samples show an interesting magnetic transition from Neel to Yafet–Kittel configuration, as the Cd^{2+}concentration is increased beyond (x = 0·4). The FT–IR spectra confirm the formation of the metal oxide bond as they exhibit two wave number bands in the range of (595 cm^{-1} and 450 cm^{-1}), corresponding to the tetrahedral and the octahedral stretching vibrations of the metal oxide, respectively. The structural evolutions of the Nano phase investigated using powder X-ray diffraction (XRD) technique show that the average crystallite size is (35 nm). The magnetic studies reveal that the saturation magnetization, Ms, increases up to (x = 0·4) and decreases when the value of (x is >0·4). It is proposed that the incorporation of Cd^{2+} ion takes place into the tetrahedral sites and up to (x = 0·4), Neel's model is followed. But for (x > 0·4), canting of spins occurs, as explained by Yafet–Kittel (Y–K) model. The d.c. resistivity decreases as a function of temperature.

S. Xavier et al. (2013) [19] the neodymium substituted cobalt ferrite having general molecular formula $CoNd_xFe_{2-x}O_4$ (for x= 0.0to 0.25) have been prepared by sol-gel auto combustion technique. X-ray diffraction analysis confirmed the formation of spinel structure in all the samples. The lattice parameter and crystallite size of the samples increase with the

increase in the concentration of neodymium. The FTIR spectrum analysis indicates the substitution of Fe^{3+} ions on octahedral sites by Nd^{3+}ions. Transmission electron microscope observations revealed that the neodymium doped cobalt ferrite nanoparticles were roughly spherical and slightly agglomerated.

J.B. Mote et al. (2014) [20] in this work zirconium (Zr^{4+}) substituted cobalt ferrite Nano crystalline ferrites having the formula, $Co_{1+x}Zr_xFe_{2-2x}O_4$ with (x = 0.0, 0.1, 0.2 and 0.3) have been synthesized by sol-gel auto combustion method. Citric acid ($C_6H_8O_7$) was used as a fuel; the pH was maintained at (7) and the prepared samples were sintered at (600˚C) for 4 h. The structural properties were estimated from X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) studies. The microstructural studies were investigated through Scanning electron microscopy (SEM) technique. The average particle size was calculated by using Debye Scherer's formula using XRD data and is obtained to be (14-26) nm. The average grain size was found to be in nanometer range and of the order of (16-28) nm obtained by using SEM images. The IR spectra show two principle absorption bands in the range of (400 cm^{-1} to 1000 cm^{-1}).

M. M. Lumina Sonia et al. (2014) [21] the samarium substituted nickel ferrites having a general formula $NiSmFe_2O_4$ (Sm= 0.0, 0.025, 0.050, 0.075, 0.1) have been synthesized by the sol-gel route. The samples thus obtained were analysed for their structural, morphological magnetic properties as a function of increasing Sm content. The structural analysis of all the as prepared samples was done using the (XRD) and (FTIR) studies which confirmed the formation of the single phase inverse spinal cubic structure. The crystallinity and the crystal size were found to decrease with

increasing samarium content .The surface morphology of all the samples were determined using the (SEM) analysis. Substituting samarium has a remarkable influence on the magnetic properties, which is confirmed from the magnetic measurements recorded at room temperature.

S. Kumar et al. (2014) [22] the Lanthanum substituted Mn-Zn nano-ferrite with formula $Mn_{0.6}Zn_{0.2}La_{0.2}Fe_2O_4$ has been synthesized by sol-gel auto-combustion technique. X-ray diffraction confirmed the formation of single phase spinel structure. Particle size was found to increase, (11.1-18.5) nm, with increase in temperature. (TEM) has been used to justify the shape and particle size with (XRD). The dc resistivity of Nano ferrite was studied as a function of temperature which indicates the semiconducting nature of Nano ferrites. Further, high value of dc resistivity (~10^7 Ω-cm) was observed. Various theories and models have been used to authenticate the structure and electrical results.

1.8 Aim of the Present Work

1- Preparation of ceramic materials, substituted with cobalt ferrite series ($CoLa_xFe_{2-x}O_4$) where x takes values (0.0 to 0.30) by (sol - gel) chemical method.

2- Studying the structural properties (the crystal size, lattice constant and density) of powders and the affected of the calcination temperature and the concentration of Lanthanum at different temperatures.

3- Studying the electrical properties (dielectric constant, resistivity and conductivity of all prepared samples), and the effect of the frequency on the previous properties at different calcination temperatures.

4- Determine the appropriate condition for the prepared samples.