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Structural ,Morphological, Electrical and Dielectric properties of Li-Zn Nanoferrites

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الخواص التركيبية, المجهرية, العزلية والكهربائية لفرايت Li-Zn النانوي

رسالة مقدمة الى

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CHAPTER ONE

Introduction and Applications

1.1 Historical of Lithium Ferrite

Latterly metal-oxide nanoparticles have been the more interest subject because of their amazing optical, electronic and magnetic properties, which often differ from the bulk[1]. The Ferrite expression is used to point out to all magnetic oxides containing iron as main metallic component. Ferrites are very attractive materials because they simultaneously show high resistivity , high saturation magnetization, and attract now a huge attention [2].

Ferrites can be characterized by high magnetic permeability, high resistivity up to $10^9 \Omega$, dielectric constant between(10-15). This amounts change with electric field. Ferrite can be classify as Ferrimagnetic material semiconductor.[3].

The magnetic property of the ferrite is due to the formation and the distribution arrangement of the ions in the sub lattice. one of ferrites types is spinal ferrites and are most widely used family of ferrites which are called cubic ferrites. Its high electrical resistivity and low eddy current losses make them ideal for use at microwave frequencies. The spinel structure of ferrites as possessed by mineral spinel $MgAl_2O_4$ was first determined by Bragg and Nishikawa in 1915[4].

Most of the ferrite have a spinel structure with a formula AB_2O_4 , where “A” are divalent ions such as Mg^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , and “B” are the trivalent ions such as Fe^{3+} and Al^{3+} . Spinel structure has an oxygen ion sub lattice, in a cubic close-packed arrangement with cations occupying various combinations of the octahedral (O) and tetrahedral (T) sites. [5].

Spinel ferrites can be classified into three categories, viz. normal, inverse and mixed ferrites based on site occupancy by divalent and trivalent metal ions. In normal ferrites all the tetrahedral sites are occupied by the eight divalent cations and the octahedral sites by the sixteen trivalent metal ions, in inverse ferrite eight out of the sixteen trivalent metal ions occupy tetrahedral sites, and the octahedral sites are occupied by eight divalent metal ions and the remaining eight trivalent cations. Mixed ferrite is a kind of ferrites, which is neither completely normal nor inverse since the A, and B sites are randomly occupied by both divalent and trivalent metal ions, its good electromagnetic materials and they have been used in various technological devices .

One of the ferrite kinds is lithium ferrite ($\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$) which possesses a spinel structure is a material of extensive study both in its pure and in its substituted form. They are found to be used in certain applications like magnetic components, microwave devices such as isolators, circulators, gyrators and phase shifters, memory core, power transformers in electronics, antennae, etc. lithium ferrites and substituted lithium ferrites have certain interesting properties like high D.C resistivity, high Curie temperature, high and wide range of saturation magnetization and low losses. These properties are very important for application point of view. Ferrites properties are strongly dependent on various factors like nature and amount of the substituent, process of synthesis, sintering conditions etc. [6,7].

Zinc substitutions in lithium ferrite are known to make an enhance in in the magnetization for low levels of substitution (under $x = 0.3-0.4 \text{ Zn}$) followed by a decrease in magnetization for larger amounts. This is generally explained by a magnetic dilution of the A-sub lattice with zinc

which initially causes the net magnetization to increase with x , due to the dominance of the B-sub lattice [8].

1.2 Literature review

At the first half of the twentieth century several major studies have been done by different researchers in different parts of the world about the development of magnetic materials began in Japan by researchers V. Kato, T. Takei, and N. Kawai in the 1930 and by J. Snoek of the Philips Research Laboratories in the period 1935-1945 in the Netherlands. Snoek in 1945 had laid down the basic fundamentals of the physics and technology of practical ferrite materials [9].

*Adolph. et al.(1970)[10]studied a new process for preparing coprecipitated lithium containing ferrites. Chemical coprecipitation results in a fine particle powder which, if properly sintered, yields fast switching memory cores. Ferrites containing Fe, Mn, Ni, Zn, etc., are readily co precipitated because of the insolubility of their hydroxides and oxalates. lithium because of its solubility cannot be precipitated as a hydroxide or oxalate in an aqueous solution, but it was found that it can be coprecipitated in the form of a stearate from an ammonium or tetra methyl ammonium hydroxide-stearic acid solution. The other elements are coprecipitated from the solution as hydroxides. The stearate is burned from the dried precipitate powder, leaving a ferrite with a specific surface area of $40 \text{ m}^2/\text{g}$. The switching speed of cores fabricated from coprecipitated lithium manganese ferrite is improved compared to cores prepared by the mixed oxide process but only at the expense of a higher drive.

*Rezlescu et al. (1998) [11] studied the influence of R_2O_3 substitution on the structure, magnetic and electrical properties of LiZn ferrite, the results obtained revealed that by introducing a relatively small amount of R_2O_3 ($R=Yb, Er, Dy, Tb, Gd$ and Sm) instead of Fe_2O_3 which is an important modification of both structure and properties that can be obtained. R_2O_3 facilitates the formation of the secondary phases (orthoferrite, garnet) on the grain boundary which suppress the abnormal grain growth. The R ions tend to flatten the $m-T$ curves, shifted the Curie point to lower temperature and increased the electrical resistivity. The effects of rare-earth ions were correlated with their ionic radius which changes from 0.86 \AA in Yb to 1.0 \AA in Sm.

* Cho et al. (1999) [12] used chemical synthesis technique that uses poly acrylic acid (PAA) to prepare nanocrystalline $Li_{0.3}Zn_{0.4}Fe_{2.3}O_4$. Phase-pure spinel that had an average particle size of 13 nm which was synthesized at a low temperature (450°C) for 30 min. The average particle size was dependent on the firing temperature and amounts of PAA and Bi_2O_3 . The combustion reaction of PAA was believed to be the main reason for the low-temperature synthesis of nanocrystalline lithium zinc (Li-Zn) ferrites. In addition, a chelating tendency was observed, via infrared (IR) spectroscopy, in the dried gel precipitates that were prepared at a low pH (2). The initial densification behavior of the nanopowder compacts was studied using linear-shrinkage data. Densification of the nanopowder without Bi_2O_3 started at low temperatures (400°C). The addition of Bi_2O_3 to the nanopowder noticeably did not contribute to reducing the initial densification temperature. This result was supported by the activation-energy calculation for the initial densification. Compared to an activation energy of 280 kJ/mol for grain-boundary

diffusion of the nanopowder without Bi_2O_3 , a higher value (430 kJ/mol) was obtained in the case of the 3 wt% Bi_2O_3 -containing nanopowder.

*Hessien.(2008)[13]synthesized Nanocrystalline lithium ferrite (LiFe_5O_8) powders by oxalate precursor route method and studied effects of $\text{Fe}^{3+}/\text{Li}^+$ mole ratio, and annealing temperature on the formation, crystalline size, morphology and magnetic properties systematically studied. The $\text{Fe}^{3+}/\text{Li}^+$ mole ratio was controlled from 5 to 3.33 while the annealing temperature was controlled from 600°C to 1100°C . The resultant powders were investigated by differential thermal analyzer (DTA), X-ray diffractometer (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). DTA results showed that LiFe_5O_8 phase started to form at around 520°C . XRD indicated that LiFe_5O_8 phase always contained $\alpha\text{-Fe}_2\text{O}_3$ impurity and the hematite phase formation increased by increasing the annealing temperature X850 1C for different $\text{Fe}^{3+}/\text{Li}^+$ mole ratios 5, 4.55 and 3.85. Moreover, lithium ferrite phase was formed with high conversion percentage at critical annealing temperature $750\text{--}800^\circ\text{C}$. Single well crystalline LiFe_5O_8 phase was obtained at $\text{Fe}^{3+}/\text{Li}^+$ mole ratio 3.33 and annealing temperatures from 800°C to 1000°C . Maximum saturation magnetization (68.7 emu/g) was achieved for the formed lithium ferrite phase at $\text{Fe}^{3+}/\text{Li}^+$ mole ratio 3.33 by annealing temperature 1000°C .

*Ibetombi Soibam et al. (2009) [14] studied series of Co substituted lithium zinc ferrite powders with different content of Co (0.00 to 0.1 in steps of 0.02) were prepared by a novel sol-gel auto combustion process using citric acid. The spinel structure of the sample was confirmed by XRD. The variation in lattice parameter and density with cobalt concentration was studied which showed an increasing trend. A decreasing pattern was observed in variation of porosity with increasing

Co. Room temperature dielectric constant and resistivity were studied as a function of composition at 10 KHz. Their results showed that the room temperature dielectric constant decreases with successive addition of Co^{2+} in the series. The observed variation in dielectric constant had been explained on the basis of space charge polarization and Koops two layer model. Resistivity is observed to increase with increasing concentration and the observed variation in resistivity had been explained by Verwey hopping mechanism.

Ruiz et al. (2012)[15] presented the results of the effect of Al substitution on the magnetic and electrical properties of $\text{Li}_{0.2}\text{Zn}_{0.6}\text{Fe}_{2.2-x}\text{Al}_x\text{O}_4$ ferrites ($0,0 \leq x \leq 0.5$) prepared by the standard ceramic technique. The characterization has been performed by using XRD, SEM, magnetic and dielectric response in frequency. XRD. analysis confirmed that the system exhibits polycrystalline single phase cubic spinel structure only for low dopant content. Doping decreases the dielectric loss tangent and the ferrite conductivity was more than two orders of magnitude in the whole analyzed frequency range. Attenuation has a maximum intensity(86dB) near 90 MHz for $x= 0.4$. The wider bandwidth at 20 dB(94.6 MHz) was for $x= 0.3$.

* Borhan · K. Gheisari(2013)[16] synthesized nanocrystalline Li–Zn ferrites with the chemical composition $\text{Li}_{0.5}\text{Zn}_x\text{Fe}_{2.5-x}\text{O}_4$ (where $x= 0, 0.1, 0.2, 0.3, 0.4, 0.5$) by the glycine– nitrate process using glycine as a fuel, nitrate as an oxidizer and microwave oven as a heat source.the combustion reaction was studied by differential thermal analysis and thermogravimetry.the experimentally determined combustion reaction is extremely exothermic and it occurred at 170°C . The as-synthesized powders were characterized by X-ray diffraction technique. X-ray diffraction data showed that nanocrystalline Li–Zn ferrite powders with a

spinel structure have been formed successfully in all samples. Morphological studied using scanning electron microscopy and field emission scanning electron microscopy showed agglomerated clusters with a lot of pores attributed to the large amount of gases released during the combustion synthesis with the particle size of 20–40 nm. The magnetic measurements on the as-synthesized powders and compacted samples were carried out by using a vibrating sample magnetometer and an inductance /capacitance /resistance meter, respectively. Saturation magnetization increases with the increase in zinc concentration up to $x=0.2$ and then it decreases with the increase in the zinc content. In addition, maximum magnetic permeability also obtained for the sample with $x=0.2$ at different frequencies.

* Mazen and Abu-Elsaad. (2013) [17] synthesized Lithium ferrite by milling process. The powder was annealed at four different temperatures 600, 800, 1000 and 1200 °C. The α - Fe_2O_3 formed in single-phase cubic spinel structure the powders annealed at 800 °C. Particle size of lithium ferrite is in the range was 26–70 nm, it was dependent on the annealing temperature. The saturation magnetization increased from 22 to 85 emu/g and the coercivity decreases from 124 to 4 Oe with increase in the annealing temperature. The dielectric constant (ϵ'), dielectric loss ($\tan \delta$) and ac conductivity (σ_{ac}) were measured at room temperature as a function of frequency. The results of dielectric properties were explained in terms of Koops phenomenological theory.

*Rashad et al.(2015)[18] synthesized Nanocrystalline lithium ferrite LiFe_5O_8 powders by the sol gel auto-combustion method from the corresponding metal nitrates using urea as a fuel. DTA results showed that the LiFe_5O_8 phase started to form temperature around 385°C X-ray diffraction analysis indicates that all compositions were formed in a

single-phase cubic spinel structure at different annealing temperatures from 400 to 800 °C for 2h. The lattice parameter was found to decrease where as the particle size was increased with annealing temperature. The frequency exponent “s” of lithium ferrite lied in the range 0.5 to 1, which confirmed the electron hopping between Fe^{2+} and Fe^{3+} ions. The electron mobility in LiFe_5O_8 samples ranged from 0.05 to 0.29 eV, which clearly indicated that the present lithium ferrites have semiconductor-like behavior. The saturation magnetization was increased with increasing the annealing temperature up to 800°C. High saturation magnetization ($M_s=51.9$ emu/g) was achieved for the ferrite powders produced at annealing temperature 800°C for 2 h.

1.3 Aims of Study

1-To preparing substituted zinc with ferrite series ($\text{Li}_{0.5-0.5x} \text{Zn}_x \text{Fe}_{2.5-0.5x} \text{O}_4$) where x takes values (0.0, 0.3, 0.6, 0.9) by modern (sol - gel) chemical method.

2-To Know the structural properties (crystalline size, lattice constant and density) of powders and the influenced of the calcination temperature to change the phases, all these by X-ray diffraction and identify other structural properties by using (FTIR, SEM and AFM).

3-To find out the dielectric Properties, dielectric constant and A.C conductivity for the prepared samples and the effect of the frequency for all samples.