AN OVERVIEW ON STRUCTURAL AND MAGNETIC PROPERTIES OF CERTAIN SUBSTITUTIONS IN COBALT FERRITE

A. M. Shahare[1], M. S. Bisen[2] , A. V. Bagde[3], D. S. Choudhary[1]
*1Dhote Bandhu Science College, Gondia, Dist - Gondia (M.S.) India
2Yashwantrao Chawhan Arts, Com. and Science College, Lakhandur, Dist-Bhandara (M.S) India
3 Chintamani College of Science, Pombhurna, Dist - Chandrapur (M.S.) India

ABSTRACT

Ferrites have become immensely important materials - technologically and commercially accounting for the bulk of global demand in manufacturing, processing and applications. The present paper focuses on the brief review of structural and magnetic properties of CoFe2O4 with permutations of Zn, Ni, Cu, Mg and some rare-earth (RE) metals. It is observed that the dopant concentration affects the particle size and by varying the degree of substitution, the magnetic properties of fine particles can be speckled due to influence of cationic distribution and their occupancy in specific sites. Over the last decades, the cobalt-RE-magnet alloys have emerged with high permanent magnetic properties. The different RE ions doped with small amount in CoFe2O4 increases porosity, coercivity, magnetization with decreased grain size. With aiming to investigate the effect of substitution, the overview may be fruitful for reconnoitering the newer tailor materials

Keywords: Ferrites, RE metals, structural and magnetic properties, porosity, coercivity

1. Introduction

Ferrites are mixed metal oxides with iron (III) oxide as main component it is a magnetic material exhibit in ferrimagnetic ordering and magnetism due to the super exchange interaction.[1]. Ferrites have wide range of applications depending upon their properties. Properties of ferrites are dependent upon several factors such as composition, method of preparation, substitution and doping of different cations, sintering temperature and time, sintered density, grain size and their distribution. The potential applications of ferrites in electronics, microwave and computer technologies have focused the attention of many research workers on these materials. Their physical properties themselves are dependent on a number of valence electrons of the divalent or trivalent metal ions of tetrahedral (A) and octahedral (B) sites. Several attempts have been made to enhance the qualities of ferrites by employing various methods. The most general method is the incorporation of same suitable nonmagnetic/diamagnetic impurities at the A or B sites. This method enables them to acquire improved electrical, magnetic and optical properties. [2,3]Ferrites can be divided into three groups based on their crystal structures: spinel ferrites, garnet ferrites and hexagonal ferrites. . An ideal spinel structure consists of a cubic close-packed (FCC) array of oxygen anions, where one eighth of the tetrahedral (A) sites and one half of the octahedral (B) sites are filled with cations. The general chemical formula for spinel ferrite is MFe_2O_4 where M is a divalent metal ion (like Mn, Zn, Fe, Ni, Mg, Co etc.). The cubic unit cell is formed by 56 atoms, 32 oxygen anions distributed in a cubic close packed structure, and 24 cations occupying 8 of the 64 available tetrahedral sites (A sites) and 16 of the 32 available octahedral sites (B sites). [4] Spinel ferrites are technologically important class of magnetic oxides because of their magnetic properties, high electrical resistivity, and low eddy current and dielectric loss. Ferrites are extensively used in microwave devices, computers, memory chips, magnetic recording media etc. [5, 6]The cobalt ferrite ($CoFe_2O_4$) possesses an inverse spinel structure. [7] Cobalt ferrite ($CoFe_2O_4$) nanoparticles are considered one of the most interesting metal-oxide materials because of their unique magnetic properties. From this reason, it has been successfully used in many applications such as high density magnetic recording, Ferro fluids technology, biomedical drug delivery, magnetic resonance imaging, data storage, biosensors, biocompatible magnetic nanoparticles for cancer treatment, and magneto-optical devices. Cobalt ferrite exhibits an inverse spinel structure with Co^{2+} in octahedral sites and Fe^{3+} equally distributed between tetrahedral and octahedral sites. Their physical properties depend on several factors such as method of preparation, chemical composition, sintering temperature and distribution of cations among the two sub-lattices: (A) tetrahedral and (B) octahedral.[8]

2. Improvement of Structural and Magnetic properties:

Structural and electromagnetic properties of the ferrite can be modified by divalent ions substitution. Generally, the divalent metal ions (M2+); Ni, Zn, Cu, Mg, Mn, Co or mixtures of these are substituted in different spinel ferrites. These substitutes have different sitting preferences for the two sites (‘A’ and ‘B’) in the spinel structure and can change many properties as an effect of modified cation distribution in the ferrite. On the basis of site distribution of M2+ ions and the strength of the exchange interaction among magnetic ions, the influence of M2+ substitutions on structural and magnetic properties can be explained.

2.1 Zn substitution

The magnetic property can be altered by the addition of the zinc. Zn2+ is used to improve electromagnetic properties as well as densification in the ferrite. It is substituted in spinel ferrite to improve magnetization. [9] Faheim AS et al.[10] synthesized nano-crystalline zinc-substituted cobalt ferrite powders, Co1-xZnxFe2O4 (X=0.0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0) by the Co-precipitation method. X-ray analysis showed that the samples were cubic spinel. The increase in zinc concentration resulted in an increase in the lattice constant, X-ray density, ionic radii, the distance between the magnetic ions and bond lengths on tetrahedral sites and octahedral sites of cubic spinel structure. The HR-TEM and XRD shows that crystallite size within the range of 6–24 nm. The magnetic measurements showed that the saturation magnetization and coercivity decrease by increasing the zinc content. Furthermore, the results reveal that the sample with a chemical composition of Co0.3 Zn0.7Fe2O4 exhibits the super-paramagnetic behavior. El-Saaey et al. [11], showed by same using same preparation method that as the zinc content increases, the saturation magnetization and coercivity decrease and lead to the super-paramagnetic behavior. Substitution of Zn ions will cause migration of Fe3+ from A-site to B-site causing an overall change of the lattice. The XRD patterns revealed that the spinel cubic structure is formed for the synthesized materials. The growth of particles is obstructed by the presence of zinc so that the average particle size decreases from 24 nm to 6 nm as the concentration of zinc is increased from X=0 to X=1. By increasing the zinc content the lattice parameter is decreased as a result of the high ionic radius of Zn2+ and the decrease in grain size. As the zinc content increases the saturation magnetization, the coercivity decreased and the best composition is about Zn=0.7.

S. Nasrin et al. [12] reported the formation of single phase spinel cubical structure. . They found that the average grain size has been increase with the sintering temperature, while it decreases with the increase of zinc content. The lattice constant is found to increase from 8.42 Å to 8.58Å with increasing zinc content and sintering temperature. The lattice constant has been found to be increases after sintering the sample at 400ºC. The saturation magnetization, remanent magnetization, coercivity and magnetic moment have been found to show a decreasing behavior with the increase of Zn content. Experimental data shows that Curie temperature has been influenced by the sintering temperature. It is also seen that the Curie temperature decreases with the increase of Zn content, while it is increases with the increase of sintering temperature.

Santosh S. Jadhav et al. [13] also confirmed the decrease in Curie temperature with increase in Zn concentration.

Coppola, P. et al. [14] found such structural and morphological changes. It shows that up to x= 0.5 zinc ions occupy preferably A-sites, above which Zn ions begin also a gradual occupancy of B-sites. TEM images show nanoparticles with different shapes varying from spheres, cubes, to octahedrons. Hysteresis loop properties are studied at 300 and 5 K. These properties are strongly influenced by the Zn and Co proportion in the nanoparticle composition. At 300 K, only samples magnetization ratio (M R/ M S) and the coercivity (HC) suggest that nanoparticles with x with high Co content present hysteresis. At 5 K, the reduced remanent < 0.5 have cubic anisotropy.

Polina Yaseneva et al. [15] reported the effect of Zn substitution on the Curie temperature. They found that Zn substitution decreases the Curie temperature (Tc), from around 440 °C for the undoped sample to ∼180 °C with x = 0.5. However, these values were also strongly affected by the pre-calcination temperature of the samples, thus TC shifts from ∼275 °C for the x = 0.3 sample to ∼296 °C after calcination at 500 °C and 800 °C respectively.G. Vaidyanathan et al. [16] studied the Co1−xZnxFe2O4 nanoparticles and showed that that the samples were cubic spinel. The average crystallite size of the particles precipitated was found to vary from 6.92 to 12.02 nm decreasing with the increase in zinc substitution. The lattice constant (ao) increased with the increase in zinc substitution. The magnetic parameters such as MS, Hc, and Mr were found to decrease with the increase in zinc substitution. M. T. Jamila et al. [17] studied the Zn content on the structural parameters. They confirmed the high degree of order and mono dispersity of nanoparticles single phase face center cubic structure (FCC). They revealed that the crystallite size were found in the range (30-70 nm) while lattice parameter, X-ray density decreases with the increase of Zn concentrations.

Swati Tapdiya et al. [18] investigated the increase of unit cell parameter ‘a’ increases linearly with increasing concentration of zinc due to larger ionic radii of Zn2+ ion and they also found the Saturation magnetization increases as Zn substitution due to the variation of exchange interaction between the tetrahedral abd the octahedral sites. Sonal Singhal et al. [19] synthesis nano particles of zinc substituted cobalt ferrite (Cox Zn 1-x Fe2 O4) where (x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0) via sol-gel method and characterized using infrared spectroscopy (IR), transmission electron microscope (TEM), X-ray diffractometry (XRD) and magnetic measurements. It is observed that the lattice parameter ‘a’ increases linearly with increase in zinc concentration. An increasing growth of grain size is also observed with increasing annealing temperature. The lattice parameter and the X-ray density, increases with increasing Zn concentration. The saturation magnetization first increases from CoFe2O4 to Co0.6Zn0.4Fe2O4 and then shows a decreasing behavior till ZnFe2O4.

A. Hassadee et al. [20] suggested that the spinel structure of Co1-xZnxFe2O4 was modified by the substitute ions. In Co1-xZnxFe2O4 , Zn2+ commonly substituted for Co2+ in the crystal structure, resulting in an increase in the lattice parameter from 8.381 to 8.412 Å. Magnetization measurements indicated that Co1-xZnxFe2O4 samples with x = 0 – 0.5 showed ferrimagnetic behavior at room temperature. The decrease in the magnetization of the Co1-xZnxFe2O4 samples from 134 to 100 emu/g and the decrease in the coercivity of the Co1-xZnxFe2O4 samples from 140 to 4 Oe by increasing the zinc content from 0 to 0.5 can be attributed to the magnetic characteristic and the anisotropic nature of cobalt. I. C. Nlebedim et al. [21] studied the temperature dependence of structural and magnetic properties of zinc substituted cobalt ferrite from 50 to 300 K. They found no observable changes in the crystal structure. At all temperatures, magnetization increased with x indicating A-site Zn substitution. Maximum magnetization obtained at 4 MA/m which decreased continuously with temperature. An inverse relation was seen between magnetic susceptibility and coercive field while a direct relationship was seen between coercive field and magnetocrystalline anisotropy coefficient.

2.2 Ni Substitution

Sonal Singhal et al. [22] demonstrated, by preparing nano-size nickel-substituted cobalt ferrites using aerosol route, that the particle size of as obtained samples was found to be ∼10 nm which increases upto ∼80 nm on annealing at 1200 °C. The unit cell parameter ‘a’ decreases linearly with the nickel concentration due to smaller ionic radius of nickel.

Won-Ok Choi et al [23] used sol gel method and investigated that when the nickel substitution was increased, the lattice constants and the sizes of particles of the ferrite powders decreased. They also observe that the nickel substitute cobalt ferrites show lower coercivity and saturation magnetization, than pure cobalt ferrite powders. These decreases are due to cation distribution, the magnetic moment, and the magneto crystalline anisotropy constant of the substituted ions. Mohd. Hashim et al. [24] observed that saturation magnetization (Ms) decreases with increase in nickel contents which is attributed to the substitution of magnetic Fe3+ ions of 5 µB by less magnetic Ni2+ ions of 2 µB. A decrease in saturation magnetization and in hyper- fine field suggests that the weakening in A and B interactions takes place due to Ni2+ substitution.

Mozaffari et al. [25] results show that a minimum calcination temperature of 500 °C is required to obtain single phase spinel structures for all the samples. It was observed that the lattice parameter of the samples decreases from 8.350 to 8.300 Å with increasing Ni content. Also mean particle sizes of the samples were obtained from FESEM images and there no relation between particle size and Ni content was found. They measured magnetic parameters carried out on cold pressed samples and found that magnetization decreases as x increases. Their results showed that Curie temperatures increases by increasing x values. They explained this change based on super exchange interactions between magnetic ions by substitution of Ni ions in Co ferrite. Also the coercive forces of the samples decreased with increasing x values which was explained by the changes in magneto crystalline anisotropy.

Nermin Kasapoglu et al [26] used the hydrothermal method at a relatively low temperature (160 ◦ C) to synthesize the Single-phase well-crystallized nano sized ferrites of Ni xCo1-xFe2O4 (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0). XRD analysis revealed that these materials belonged to the family of mixed or partially inverse spinel ferrites. They reported the decrease in magnetization as the dopant concentration of Ni2+ increased.

Abdul Gaffoor et al. [27] Synthesized nanoparticles of the composition Ni1-xCoxFe2O4 (where x=0.0, 0.2, 0.4, 0.6, 0.80 and 1.0) were synthesized at a very low temperature (180°C) by Citrate-gel auto combustion method and sintered at 5000C. They confirmed the formation of cubic spinel structure of ferrites. The crystallite size was in the range of 20nm to 31 nm that are desirable for variety of applications like, in magnetic data storage and in etc. The lattice parameter is increased with the increase of Co substitution in Ni-Co ferrites.

N. B. Velhal et al. [28] reported the formation of cubic spinel phase using the low temperature auto combustion technique. The magnetic properties indicates that as Ni content increases the Ms, Mr, Hc and Mr/Ms decreases this is due the lower magnetic moment of nickel. Also magnetic properties show the temperature dependent behavior. The values of Ms, Mr, Hc and Mr/Ms decreases with temperature. Uday Bhasker Sontu et al. [28] also prepared nickel substituted cobalt ferrite using self-combustion method at low temperatures (200oC). They reported that nickel substitution into cobalt ferrite causes the magnetic and electric properties of the ferrite to tune from hard magnetic and lower resistivity cobalt ferrite to soft magnetic and high resistiveity nickel ferrite. Ajaypal Singh et al. [30] synthesized Nanoscale ferrite particles by using solution combustion method. X-ray diffraction studies reveal the formation of single phase spinel structure. Magnetic studies show variation of coercivity and saturation magnetization with cobalt substitution and show higher coercivity and saturation magnetization than pure nickel ferrites. P.P. Hankare et al. [31] also observed the single cubic spinel phase for all the samples. The decrease in lattice parameter and increase in crystallite size of the ferrispinel was observed with increasing nickel content. The nanosize of the synthesized material lie in between 20–25 nm.

2.3 Cu substitution

A. Samavati et al. [32] results show that the increasing Cu concentration causes decrease in the nanoparticle size from ~30 to ~20 nm. Specific saturation magnetization (Ms), remnant magnetization (Mr) and coercivity (Hc) of the spinel ferrites are diminished by the substitution of Cu2+ ions.

B. Chandra Sekhar et al. [33] synthesized Copper substituted cobalt ferrite nanoparticles, Co1−xCuxFe2O4 (x=0.00–0.25) by sol–gel auto combustion method. X-ray diffraction analysis on the samples was done to confirm the cubic spinel structures and Scherrer equation was used to estimate the mean crystallite size as 40 nm. Copper substituted cobalt ferrites have shown improved strain derivative values as compared to the pure cobalt ferrite and thus making them suitable for stress sensing applications. The results have been explained on the basis of cationic distributions, strength of exchange interactions and net decreased anisotropic contributions due to the increased presence of Co2+ ions in B-sites as a result of Cu substitutions. N. Sanpo et al. [34] also reported the influence of copper substitution on the microstructure and crystal structure and particle diameter.

M. Margabandhu et al. [35] synthesized Cu2+ substituted cobalt ferrite (Co1-xCuxFe2O4, x=0, 0.3, 0.5, 0.7 and 1) magnetic nanoparticles via chemical co-precipitation method. The XRD results confirm the crystalline nature and presence of single phase cubic spinel structure of the obtained magnetic nanoparticles. The VSM results show that the magnetic parameters coercivity (Hc), retentivity (Mr) decrease with increase in Cu2+substitution and saturation magnetization (Ms) shows increment and decrement with Cu2+ substitution in CoFe2O4 magnetic nanoparticles.

Sampath KA et al. [36] prepared cobalt-copper mixed ferrite having the composition Co1-xCuxFe2O4 (x=2, 4, 6 and 8) by SHS. They have studied the sample Co0.2Cu0.8Fe2 O4 demonstrated the mixed spinel ferrite phase. They reported that the sample represented a very much closer linearity of the curve for the softest one. Therefore, it was found to be an appropriate soft ferrite for hyperthermia application.

Rakesh K. Singh et al. [37] synthesized copper substituted cobalt ferrite nanoparticles using citrate precursor method. The precursor was annealed at temperatures 700°C. They found that compound possess a cubic spinel structure. The lattice parameters of all the compounds are lying between the cell parameters of CuFe2O4 and CoFe2O4. Sharp changes were observed in particle size, lattice constant, magnetization and retentivity with the increasing Cu content. The values of coercive field and retentivity are found to be small. M-H curves could not get saturated up to 10 kOe.

2.4 Mg substitution

Vithal Vinayak et al. [38] synthesized the nanocrystalline Co1-xMgxFe2O4 (x = 0.0, 0.50 and 1.0) successfully synthesized by sol-gel auto combustion technique. The X-ray diffraction results for the samples of Co1-xMgxFe2O4 (x = 0.0, 0.50 and 1.0) showed the formation of single phase cubic spinel structure. The lattice constant is found to decrease with increasing Mg2+ concentration. The particle size of the samples calculated using the Debye Scherer’s formula was obtained in the range of 11-24 nm. The tetrahedral bond length, octahedral bond length, tetrahedral edge and octahedral edges decrease as magnesium content x increases. Overall, the substitution of magnesium in cobalt ferrite influences the structural properties.

V. V. Dhole et al. [39] successfully synthesized the nanocrystalline Co1-xMgxFe2O4 (x = 0.0 and 0.25) by sol-gel auto combustion technique. The X-ray diffraction results showed the formation of single phase cubic spinel structure. The lattice constant is found to decrease with increasing Mg2+ concentration. The particle size of the samples calculated using the Debye Scherrer’s formula was obtained in the range of 12-32 nm. The average grain size determined from scanning electron microscopy technique is of the order of 45 - 66 nm.

3. Inclusion of rare earth elements:

Recently, rare earth ions substituted spinel ferrite nanoparticles has emerged as a promising strategy to improve their physical properties. The rare earth substituted cobalt ferrites found an useful in high frequency devices and power supply due to high resistivity and low dielectric losses. Rare earth ion doped into cobalt ferrites has been reported to lead to structural distortion that induces strains in the material which indicate improved crystallinity of the sample and to affect the electrical and magnetic properties significantly. Here, we are limiting our studies to certain rare earth substitutions Sm, Yt, Gd and Nd.

3.1 Sm Substitution

Rashad et al. [40] reported a change in the magnetic properties of samarium doped cobalt ferrite nanoparticles synthesized by the citrate precursor route. The results found that due to increase in addition of Sm3+ in cobalt ferrite, the value of the saturation magnetization and coercivity decreases and it is increased by increasing the calcination temperatures from 400 to 800 °C.Sheena Xavier et al. [41] investigated samarium-substituted cobalt ferrites prepared by sol-gel method and reported the formation of single-phase spinel structure without any secondary phase. It is found that the substitution of samarium in cobalt ferrite has resulted in an increase in lattice parameter and crystallite size. The saturation magnetization and coercivity decreased with an increase in samarium content. Decrease in saturation magnetization is attributed to the decrease in the net magnetic moment due to the substitution of nonmagnetic ion in the octahedral site. A larger grain size makes the motion of domain walls easier, and this may be the possible reason for decrease in coercivity with increase in samarium.

Ahmad SI et al. [42] synthesized Sm and Ce co-substituted nano crystalline cobalt ferrite, CoFe2-x-ySmxCeyO4 (x = y = 0.00, 0.5, 0.1, 0.12 and 0.25), by sol-gel combustion method and stated the spinel structure with a secondary phase of RE2O3 for higher molar concentration of rare earth ions. Increasing Sm and Ce concentrations leads to the decrease in the crystallite size and increase in specific surface area and Strain. With increase in doping of Sm and Ce, due to decrease in particle size and surface effect, Ms and Hc were found decreasing. A.K. Nikumbh et al. [43] also reported similar results when pure nanoparticles of the rare-earth substituted cobalt ferrites CoRExFe2−xO4 (where RE=Nd, Sm and Gd and x=0.1 and 0.2) were prepared by the chemical co-precipitation method. The lattice parameter increased with rare-earth content for x≤0.2. Increase in rare earth substitution in cobalt ferrite reduces the coercive force, saturation magnetization, ratio MR/MS and magnetic moments may be due to dilution of the magnetic interaction. L. Ben Tahar et al. [44] used forced hydrolysis in polyol method and prepared pure nanoparticles of cobalt ferrite doped with Gd and Sm. XRD reveals the increase in cell size with slight distortions in the spinel-like lattice indicating the entrance of RE3+ ions. A significant increase in the saturation magnetization is achieved by doping with magnetic Gd3+ and Sm3+ ions which is mainly attributed to the high magnetic moment of these cations and probably an inter-site rearrangement of the Co2+ ions.

3.2 Yt Substitution

Isaac Haïk Dunn et al. [45] investigated Yttrium-substituted cobalt ferrites prepared using the sol-gel combustion method. Decrease in the cell parameters with increasing Y 3+ has been observed. Substitution of Yttrium affect the inversion factor δ since yttrium enters the lattice in octahedral sites. Thus the samples are not perfectly inverse spinels. Both magnetization and Curie temperature decrease with the increase in doping of Y3+ content due to cation distribution and owing to a decrease in the number of Fe-Fe super-exchange interactions in the octahedral sublattice.

Swati Kumari et al. [46] have investigated structural and magnetic properties of CoFe2-x YxO4 (x = 0.0 and 0.05) compound synthesized by citrate precursor method. X-ray diffraction and Raman spectroscopy have confirmed the formation of single phase cubic spinel structure. Doping of small amount of Y3+ cation causes significant reduction in the particle size. Enhancement in coercivity and reduction in highest magnetization with the Y3+ substitution has been recorded. The enhancement of coercivity is attributed to the transition from multidomain to single domain state. The decrease of highest magnetization and magnetocrystalline anisotropy constant is ascribed to weakening of superexchange interaction and surface effect.Mossbauer spectroscopy reveals that on increasing the concentration of doped Y in cobalt ferrite, the hyperfine field strength and the isomer shift first increase and then decrease, whereas the quadrupole splitting continuously increases. [47]

M.K. Shobana et al. [48] prepared Y0.2CoFe1.8O4 nanocrystallites using a sol–gel combustion technique. The XRD peaks indicate the occurrence of pure spinel ferrite structure. Both the crystallite size and the degree of particle agglomeration increased with increasing calcination temperature, probably because of the disappearance of the polymer at high temperatures. D.M. Ghone et al. [49] reported a decrease in saturation magnetization with the increased in yttrium ions in cobalt ferrite, synthesized by chemical co-precipitation method. XRD reveals is formation of cubic spinel ferrite along with the secondary phase of YFeO3 in substituted cobalt ferrite as concentration of yttrium is increased. Magnetostriction coefficient also decreases due to interaction of nonmagnetic rare earth ion with transition metal ion.

3.3 Gd Substitution

Lin. et al. [50] prepared Co GdxFe2−xO4 (x = 0, 0.04, 0.08) by a sol-gel auto combustion method. The XRD patterns revels that the samples are single phase, no impurity peak was detected and the Gd3+ added sample is larger due to the ionic radius of Gd3+ ions (0.938 ˚A) is greater than that of Fe3+ ions (0.645 ˚ A). The increasing gadolinium does not increase monotonously the lattice parameter due to the fact of larger radius in CoFe2O4 which produce the lattice distortion. Ishtiaq Ahmad et al. [51] reported that the Co Gd2x Fe2-2x O alloy mainly consists of cubic spinal structure. Initially, lattice constant ‘a’ have small increase but for higher values of x, ‘a’ decreases due to increase anti-parallel exchange coupling. With the increase in doping concentration X-Ray density, bulk density and Porosity increases. . The Ms and Mr are found to increase with increasing Gd concentration while the corresponding Hc decreases.V. S. Puli et al.[52] found the inverse spinel cubic structure in gadolinium (Gd) substituted cobalt ferrites (CoFe2−xGdxO4; x = 0–0.3), synthesized by solid state reaction method. A considerable increase in the saturation magnetization has been observed upon the initial substitution of Gd (x = 0.1). The saturation magnetization drastically decreases at higher Gd content (x ⩾ 0.3). Increase in coercivity with increase in Gd3+ is content is attributed to magnetic anisotropy in the ceramics.

R.N. Panda et al. [53] studied of nano-crystalline CoMxFe2−xO4 (where M=Gd and Pr and x=0, 0.1 and 0.2) powders prepared by a citrate precursor technique. Saturation magnetization of the materials decreases with increasing doping concentration. Inclusion of rare-earth atoms in the crystal lattice cause increase in the grain growth and coercivity of the material. The improved coercivity compared with those for the pure cobalt ferrites is attributed to the contribution from the single ion anisotropy of the rare-earth ions present in the crystal lattice and the surface effects resulting in alteration of magnetic structures on the surface of nano-particles.R.S. Yadav et al. [54] investigated the influence of Gd3+ ion in cobalt ferrite nanoparticles on structural, magnetic, dielectric, electrical, impedance and modulus spectroscopic characteristics using sonochemical synthesis method. The average crystallite size decreases with the substitution of Gd3+ in cobalt ferrite nanoparticles. Saturation magnetization of Gd 3+ doped cobalt ferrite nanoparticles decreases with increase in Gd 3+ substitution. Pervaiz E. et al. [55] observed that Gd3+ substitution have tailored the magnetic properties of Co-ferrites due to influence on A-B exchange of electrons. Saturation magnetization, coercivity and remanance all decreases with increase in dopant concentration of Gd3+ in cobalt ferrite.

3.4 Nd Substitution

Xavier S. et al. [56] studied a series of neodymium doped cobalt ferrite samples (CoFe2-xNdxO4 with x=0.0, 0.05, 0.1, 0.15, 0.2, 0.25), prepared through the sol- gel technique. They confirmed the formation of spinel structure in all the samples. Increasing doping concentration of neodymium increases the lattice parameter and crystallite size of the samples. TEM observations revealed that nanoparticles were roughly spherical and slightly agglomerated. The saturation magnetization and coercivity decrease with increase in neodymium content which is attributed to the particle size dependence of magnetic properties in the multidomain regime.

L. Avazpour et al. [57] investigated magnetic properties of rare earth (RE) substituted cobalt ferrite Co1−xRExFe2O4; x = 0–0.2 in steps of 0.05 and RE is Nd and Eu using the sol–gel method at annealing temperatures 550° C. They found that the saturation magnetization of the ferrite materials at room temperature decreases with increase in RE inclusion. Coercivity of the rare earth substituted cobalt ferrite improved especially for 5% Neodymium substituted cobalt ferrite. This may be attributed to the fact that there is the contribution from the single ion anisotropy of the rare-earth ions present in the crystal lattice and also to the effects of a change in magnetic structures on the surface of the nanoparticles.

Yadav R et al. [58] reported the changes in magnetic properties of Nd3+ doped cobalt ferrite nanoparticles synthesized by starch-assisted sol–gel auto-combustion method. They reported that room temperature saturation magnetization and coercivity increase with addition of Nd3+ substitution in cobalt ferrite. Recently, Zhao et al. [59] observed Nd 3+ ions substituted cobalt ferrite prepared by the emulsion method. They observed the varying concentration of Nd 3+ ions increases coercivity in cobalt ferrite however, saturation magnetization decreases.

Conclusion:

The variations in the magnetic and structural properties of Cobalt ferrites were studied with increasing concentration of Ni, Zn, Cu and Mg and some rare earth metals (Sm, Yt, Gd and Nd) in the cobalt ferrite. CoFe2O4 which has got some peculiar properties like high saturation magnetization (Ms), high coercivity (Hc) and large anisotropy. Further the substitution of different divalent ions in this ferrite allows some tunable changes in its properties. It can be seen from above observation that the substitution of Zn2+, Ni2+, Cu2+, and Mg2+ and rare earth elements in Cobalt ferrite causes the modification in the structural and magnetic properties like lattice parameter, grain size, saturation magnetization, coercivity, Curie temperature etc. It is seen that increment or decrement in these properties depends on the dopant concentration, the type of dopant, sintering temperature and also on the method of preparation.

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