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Synthesis and Characterization of Cobalt (Co) doped Manganese Ferrite ($MnFe_2O_4$) Nanoparticles Co-precipitation Method

Vishal Manik More[1]
Research Scholar
Dayanand Science College, Latur, Maharashtra

Abstract : Cobalt doped Manganese ferrite Nanoparticles are developed using co-precipitation method at room temperature with variation in Co doping percentage. Structural Properties of prepared nanoparticles are investigated. Crystalline size is determined by using scherrers formula. XRD Pattern analysis shows that the Co doped Manganese ferrite have Spiral Ferrite Structure. The lattice constant is changing with increasing Co doping . The crystallite size of prepared samples are in the range of 1-4 nm.

Keywords : Crystalline Size

Introduction:

In recent years, nanomaterials fabrications and their uses are emerging as a critical technology having applications in many industrial sectors [1, 2]. Among these materials spinel ferrite structure of MFe2O4, where M represent metals such as Ni, Mn, and Zn has been studied due to electric, magnetic, chemical, and mechanical properties. They are currently used in wide application area such as Microwave devices, memory cores, low energy inductors, transformer cores, deflection yokes and many other applications [3, 4].

Among the various, ferrites, cobalt ferrites have received recent attention as because they possess excellent chemical stability, good mechanical hardness, remarkable high electrical resistivity and large permeability at high frequency in addition to being cost effective [5,6]. Many methods have been used to synthesize manganese ferrite nanoparticles , such as sol-gel [7], thermal decomposition [8], Solvo-thermal [9], microemulsion [10] and co-precipitation [11].the synthesis routes, co-precipitation is one preferred method due to its simplicity, low cost, high yield, is to control particle size, processibility at lower temperature and environmentally friendly synthesis route [11,12,13]. However, the magnetic nanoparticles as obtained from this method normally aggregate, thus altering magnetic properties. Therefore, the functionalization and

modification such as using metals, polymer coating and surfactants absorption on the surface, have been found to reduce the aggregation [14, 15, 16].

Manganese ferrite is a "kind of magnetic materials with cubic spinel structure" which have been extensively used in various technological applications. The properties of manganese ferrites highly depend on the composition, morphological and size which are strongly connected with preparation condition.In $MnFe_2O_4$ structure where the ionic distribution of spinels is often written as $(Mn_{1-x}Fe_x)$ $[Mn_xFe_{2-x}]O_4$ with the elements in the parentheses and the square brackets lodge in tetrahedral and octahedral sites formed by the oxygen ions respectively. In this work we have synthesized the pure $MnFe_2O_4$ and Co doped $MnFe_2O_4$ ferrite with 1%, 2%,3%,4%,5% Co doped nanoparticles via co-precipitation method and we have studied its structural properties.

Manganese ferrite ($MnFe_2O_4$): An example of spinel ferrites

Spinel ferrites are the most widely used and investigated ferrites. In recent years, research on ferrites (spinel) has been increased owing to their potential in various fields especially in biomedical field. Spinel ferrites are being employed in many biological applications because of their magnetic and electrical properties. Magnetic properties can be engineered according to need of application and it can be modified by several ways. Properties of spinel ferrite can be controlled by pH, stirring time and speed, fuel and preparative parameters used. Another name for spinel ferrites is cubic ferrites as structure of spinel ferrites is closely packed with cubic. The general formula of spinel ferrites is $Me^{II}Fe_2^{III}O_4$, in which,Mn is metal cation like Mn, Co, Fe, Cu, Cd, Mg, which are divalent and Fe represents iron cation, which are trivalent.The extensive differences in electrical, structural and magnetic properties are because of cations of non-identical valence. Spinel structure is a member of Fd3m space group. The constituents of unit cell (cubic) is configured by 56-atoms, out of these 32-oxygen anions, which are scattered in close loaded structure and 24-cations holding 8-tetrahedral sites of available 64-tetrahedral sites and 16-octahedral sites of available 32-octahedral sites.

Cation distribution can decide whether spinel is inverse, partially inverse or normal. In normal spinel, tetrahedral sites are located by 8-bivalent cations and octahedral sites located by 16-trivalent cations. $ZnFe_2O_4$ and $CdFe_2O_4$ are two examples of normal spinel ferrites. In inverse spinel, 8-bivalent cations hold 8- octahedral sites and 16-trivalent cations are scattered between 8-tetrahedral and 8- octahedral sites. $MnFe_2O_4$, $NiFe_2O_4$ and $CoFe_2O_4$ are 3 examples of inverse spinel ferrites. The value of i is equal to 0 for normal spinel and i is equal to 1 for inverse ferrite. For partially inverted ferrite, the value of i is greater than 0 or less than 1. $CuFe_2O_4$ and $MgFe_2O_4$ are two examples of partially inverted ferrite.

Chemicals used:

Cobalt doped manganese ferrite nanoparticles were successfully synthesized by using Manganese acetate tetra hydrate and ferric nitrate nanohydrate with sodium hydroxide. All the chemicals used in the experiments were of analytical reagent grade and used as same without further purification.

Sr. No.	**Chemicals**	**Linear formula**	**Molecular Weight**	**Purity**	**Purchased from**

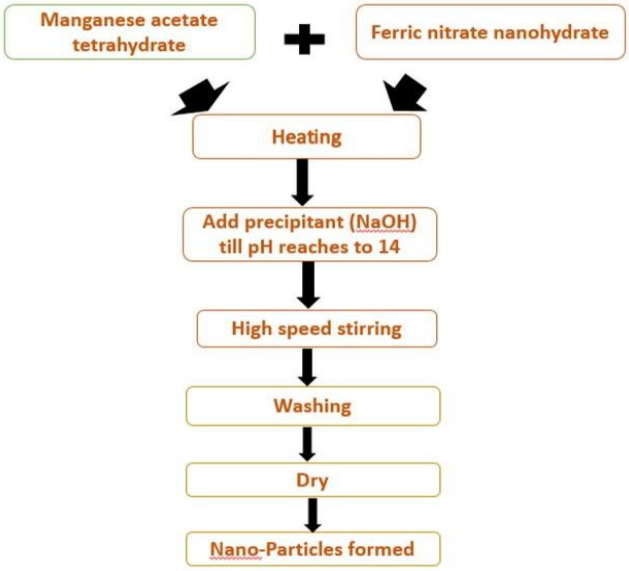
1	Manganese Acetate Tetra hydrate	**C4H6MnO4.4H2O**	**245.09**	**99.99%**	**Himedia**
2	Ferric nitrate Nanohydrate	**Fe(No3)3.9H2O**	**404.0**	**99.99%**	**Himedia**
3	Cobalt Acetate	**(CH3COO)2Co4H2O**	**249.09**	**99.99%**	**Himedia**
4	Sodium Hydroxide	NaOH	**40**	**99.99%**	**Molichem**

Synthesis of Manganese Ferrite Nanoparticles:

The basic principle for the synthesis of nanomaterials is to produce a large number of nuclei and to inhibit the growth and aggregation of grains. The nanomaterial's are usually prepared by the top down or bottom-up approach. In a top-down process, a bulk material is taken and subsequently fragmented to yield a nanoscale structure in precise patterns by way of physical, chemical or mechanical process. Although the top-down approach are simple and cost effective, but it suffers from drawbacks, i.e. It is difficult to control the size and shape of the particles and It produces imperfection of the surface structure. In the bottom up approach, it starts with molecular levels which assemble themselves chemically and it can be controlled by the reaction parameters. The nanomaterials obtained through the bottom up approach have less defects and imperfection. The bottom-up approach offer much more flexibilities in creating nanomaterials with controlled size, shape, composition and physical properties. The nanostructures made from this process are in a state of closer to a thermodynamic equilibrium state due to the reduction of Gibbs free energy. This kind of approach includes various chemical processes such as, co-precipitation method, sol-gel method, hydrothermal method, citrate precursor method, reverse micelle method etc. They are adopted more frequently for synthesizing nanocrystalline materials. Chemical synthesis processes consists of nucleation and growth steps which affects particle size and their distribution. In the present thesis, ZnO nanoparticles were synthesized using co-precipitation method.

Co-precipitation Method

The principle involved in this technique is the precipitation of metal ions with oxygen ions in the solution. For synthesis of pure $MnFe_2O_4$ nanoparticles firstly solutions of 0.5 M Manganese acetate Tetra hydrate and Ferric nitrate nanohydrate and 0.5M sodium hydroxide was prepared in distilled water. Manganese ferrite solution was stirred for 30 minutes on a magnetic stirrer to get a homogeneous solution. This was followed by drop wise addition of appropriate amount of 1.5 M Sodium hydroxide under vigorous stirring for 1 hour. A soil color precipitate was obtained which was separated by centrifugation and washed with distilled water. The precipitate was dried in oven at 80^0 C for 4 hours to get powder sample. The sample was then calcined at 400^0 C for 4hrs in a furnace to get the resultant material



Results and Discussion:

The X-Ray Difraction pattern of pure and cobalt doped $MnFe_2O_4$ nano-particles are shown in following figure. X-ray diffraction pattern it is observed that the intensive peaks corresponds to (111), (220), (311). From This diffraction peaks prepared samples have and cubic crystal structure without extra impurity.

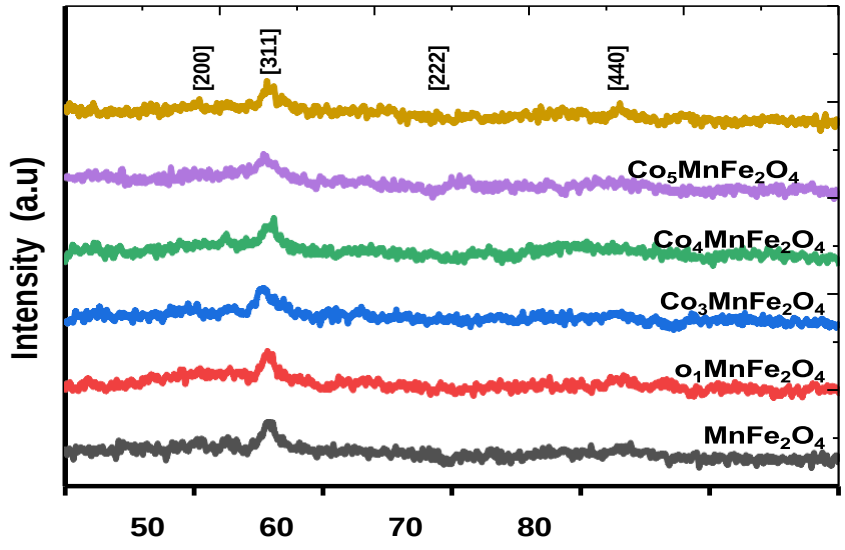
The lattice parameter was determine following relation .

$$a = d\sqrt{h^2 + k^2 + l^2}$$

Where,

a = Lattice Constant

d = Interplanar distance (hkl) = Miller Indices



2θ (Degree)

Fig: XRD Graph Of Pure $Mnfe_2O_4$ and Co-$Mnfe_2O_4$

The diffraction peaks of intensity goes on decreasing with increasing cobalt doping. The lattice parameter, volume, crystalline size, strength and tabulated.

In additional the volume of unit cells are change with increasing cobalt doping. The crystalline size was determine using schirrer formula

Crystalline Size

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

Where, k = Shape Factor

k = X-ray wavelength

β = Full Width Half Maxima θ = Braggs Angle

The crystalline size of prepared nano-particles are in the range of 1.8 to 2.4 nm. The strength is also calculated using following formula

$$\varepsilon = \frac{\beta}{4\ tan\theta}$$

The strain is also decreasing with all increasing cobalt doping it may be crystalline size. From the structural parameter it was observed that the cobalt doped in Mnfe2O4 .

Table 1: Diffraction angle, full width half maxima and d spacing for (311) plane of cobalt doped MnFe2O4 nanoparticles.

Sample	**2Θ(deg)**	**FWHM (deg)**	**d Spacing**
Mnfe2O4	36.04	2.94	2.49
1% Co-Mnfe2O4	35.85	2.45	2.503
2% Co-Mnfe2O4	35.47	2.69	2.529
3% Co-Mnfe2O4	36.14	3.20	2.483
4% Co-Mnfe2O4	35.73	4.00	2.511
5% Co-Mnfe2O4	36.18	6.10	2.481

Table 2: Lattice parameters, volume of unit cell, crystallite size, strain and dislocation density for (311) plane of cobalt doped $MnFe_2O_4$ nanoparticles.

Sample	Lattice parameter (a) Å	Volume (V) $Å^3$	Crystallite size (D) Å	Strain (Ɛ)	Dislocation density (δ) $10^{17}\times Å^{-2}$
Mnfe2O4	8.2583	563.21	28.41	0.0394	1.238
1%Co-Mnfe2O4	8.3015	572.09	34.08	0.0330	0.860
2%Co-Mnfe2O4	8.3877	590.11	31.00	0.0367	1.0401
3%Co-Mnfe2O4	8.2351	558.49	26.11	0.0427	1.4662
4%Co-Mnfe2O4	8.3280	577.60	20.86	0.0541	2.2964
5%Co-Mnfe2O4	8.2285	557.14	13.70	0.0814	5.3268

Table 3 : Values of 2θ (deg), d (ang.), FWHM for pure and Co doped $Mnfe_2O_4$ nanoparticle annealed at 400^0c.

1. Peak list of Pure Mnfe2O4

Sr. No.	2-theta (deg.)	d (ang.)	FWHM (deg)
1	**25.71(13)**	**3.463(17)**	**11.5(3)**
2	**36.04(7)**	**2.490(5)**	**2.94(15)**
3	**42.8(2)**	**2.112(11)**	**10.0(5)**
4	**63.4(2)**	**1.466(5)**	**11.4(5)**

2.Peak list Of Co 1%

Sr. No.	2-theta (deg)	d(ang.)	FWHM (deg)
1	**19.45(17)**	**4.56(4)**	**3.7(3)**
2	**30.0(3)**	**2.97(3)**	**8.6(3)**
3	**35.85(6)**	**2.503(4)**	**2.45(12)**
4	**42.9(5)**	**2.10(2)**	**7.1(7)**
5	**63.39(9)**	**1.4662(18)**	**4.21(19)**

3.Peak list of Co 2%

Sr. No.	2-theta (deg)	d (ang)	FWHM (deg)
1	22.27(11)	3.989(19)	7.5(3)
2	30.04(10)	2.972(10)	4.0(3)
3	35.47(3)	2.529(2)	2.69(14)
4	42.58(16)	2.121(8)	8.6(3)
5	62.91(12)	1.476(3)	4.3(3)

4.Peak list of Co 3%

Sr. No.	2-theta (deg)	d(ang.)	FWHM (deg)
1	21.9(3)	4.06(6)	7.9(4)
2	36.14(11)	2.483(8)	3.2(2)
3	38.6(11)	2.33(6)	2.9(19)
4	43.4(2)	2.085(9)	9.1(5)
5	58.4(60	1.580(14)	4.9(9)

5.Peak list of Co 3%

No.	2-theta (deg)	d (ang)	FWHM (deg)
1	22.5(2)	3.94(4)	8.3(3)
2	35.73(11)	2.511(8)	4.0(2)
3	43.09(19)	2.098(9)	6.6(6)
4	61.3(3)	1.512(6)	6.3(9)
5	64.0(5)	1.454(9)	3.5(14)

6.Peak list of Co 5%

No.	2-theta(deg)	d(ang)	FWHM (deg)
1	36.18(17)	2.481(11)	6.1(4)

2	**43.7(6)**	**2.07(3)**	**6.2(19)**
3	**45.3(3)**	**2.002(13)**	**5.6(10)**
4	**58.8(5)**	**1.569(12)**	**5.2(6)**
5	**63.02(11)**	**1.474(2)**	**1.1(2)**

Conclusions

1. Pure and Co doped $Mnfe_2O_4$ nanoparticles were successfully synthesized using co-precipitation method at room temperature. All prepared samples were characterised using x-ray diffraction technique.
2. From X-ray diffraction pattern of pure and Co doped $Mnfe_2O_4$ nanoparticles have cubic crystal structure upto 5% cobalt.
3. From X-ray diffraction data, the lattice parameter and volume are determined.
4. From this result, it was observed that the lattice parameter of cobalt doped $Mnfe_2O_4$ nanoparticle was smaller than of pure $Mnfe_2O_4$ samples.

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