

Review On Cobalt-Zinc Mixed Spinel Ferrite: Synthesis and Magnetic Properties

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Abstract: *Nanoparticles of Co-Zn mixed spinel ferrites have been prepared by a controlled co-precipitation method. The particle sizes of the mixed spinel ferrite may be controlled with Zn substitution since the rate of increase in particle sizes slowed down with increase of Zn content. Alteration of magnetic properties of Co-Zn mixed spinel ferrites was observed with the variation of Zn concentrations.*

Keyword: *Nanoparticles, Mixed spinel Ferrite, Chemical co-precipitation method, Co-Zn ferrites. Magnetization.*

1. Introduction:

Novel magnetic properties of these nano-materials make them highly suitable for applications in magnetic storage devices and other technological applications [1-4]. Nanoparticles of mixed spinel ferrites comprise an important class of magnetic materials having large and interesting deviations of electronic, magnetic and nuclear properties from that of their bulk counterpart [5-7].

Cobalt ferrite is an inverse spinel where all the Co^{2+} magnetic cations occupy the octahedral (B) sites and Fe^{3+} ions equally occupy both tetrahedral (A) and octahedral (B) sites. This results in antiferromagnetic spin arrangement due to strong A-B exchange interaction compared to A-A or B-B exchange interactions. Due to the unbalanced spin magnetic moments of A and B sites cobalt ferrite is ferrimagnetic in nature. Cobalt ferrite having very high coercivity (~ 5400 Oe) high cubic magnetocrystalline anisotropy, moderate saturation magnetization (~ 80 emu/g) and also its mechanical hardness and high chemical stability, is a promising material for use in the production of isotropic permanent magnets, magnetic recording media [8, 9] and magnetic fluids [10,11]. Due to high magneto-crystalline anisotropy energy of Co-ferrite, superparamagnetic relaxation could not be observed in the case of bigger size particle at room temperature. But magnetic properties like magnetic anisotropy, coercivity and onset of superparamagnetism of cobalt ferrite can be tailored by incorporating diamagnetic zinc cation into its face centered cubic spinel lattice as it modifies the A-B exchange interaction. Zn^{2+} cations in cobalt ferrite normally occupy A sites in the spinel lattice replacing magnetic Fe^{3+} cations (which eventually go to B sites). Thus due to the substitution of Zn^{2+} cations and consequent rearrangement between diamagnetic and spin magnetic moments, the system becomes magnetically diluted as $\text{Fe}_A\text{-O-Fe}_B$ interaction becomes weak which leads to many interesting properties like spin glass or cluster glass like behaviors [12].

2. Synthesis of Co-Zn Ferrite nanoparticles:

Nanocrystalline Co-Zn mixed spinel ferrites may be prepared by different methods such as controlled co-precipitation method [13], sol-gel method [14], hydrothermal techniques [15] have been widely used. S. Dey et al. [16] prepared $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ ferrite nanoparticles by coprecipitation method where a mixed solution of stoichiometric amounts of CoCl_2 , ZnSO_4 and $\text{Fe}(\text{NO}_3)_3$ was prepared and was added dropwise from a burette into a NH_4OH solution, maintaining the pH at 8 adding dilute NH_4OH from another burette. The resultant mixture was boiled at 80°C for 30min and then allowed to settle. The precipitate was filtered, washed with de-ionized water several times and then

dried in vacuum (0.05 Torr) at room temperature. The dried precipitate was sintered at various temperatures between 393 and 1173 K for 12 h. R. Arulmurugan et al. [17] prepared $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.1-0.5$) by coprecipitating aqueous solutions of CoCl_2 , ZnSO_4 and FeCl_3 in their respective alkaline medium. The mixed solutions of CoCl_2 , ZnSO_4 and FeCl_3 in their respective stoichiometry kept at 80°C (e.g. 50 ml 0.5M CoCl_2 , 50 ml 0.5M ZnSO_4 , 100ml 1M FeCl_3 in case of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and similarly for the other values of x) was added to the boiling solution of NaOH (0.64M dissolved in 1300 ml of distilled water) within 10s under constant stirring and the solutions were maintained at 95°C for 1 hr. to transform metal salts into hydroxide and hydroxide into the ferrite form.

3. X-ray diffraction and TEM analysis:

X-ray diffraction by solids is a scattering process in which the scattered waves from a large number of atoms are coherently accumulated to give the diffraction pattern. Since atoms in a crystal lattice are arranged periodically, the x-ray scattered by the scattering centers (atoms of a crystal) have definite phase relations between them and these phase relations are such that only in certain directions which will have constructive interference. Diffracted beam composed of the scattered x-rays can be obtained only when certain geometrical considerations of the atomic structures are satisfied. In three-dimensional crystals, X-ray diffraction occurs only when the wavelength of the x-ray is comparable to the distance between the scattering centers in the crystal lattice structure. The condition is explained by Bragg's law given by the equation (1),

$$2d\sin\theta = n\lambda \quad (1)$$

Here d is the interplanar distance, θ is the angle of diffraction, n is the order of diffraction and λ is the wavelength of the incident x-ray. Figure 1 shows a schematic diagram of X-ray diffraction from a set of lattice planes with inter planar distance d .

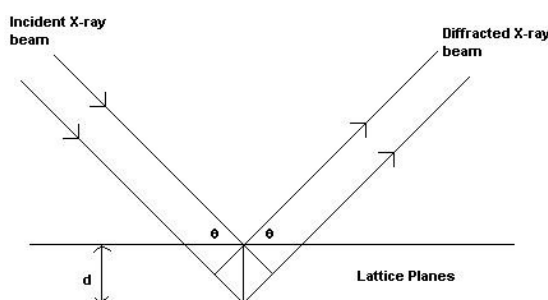


Figure 1. X-ray diffraction from a set of lattice planes.

Depending on whether the wavelength of X-ray radiation and angle of diffraction is varied or kept fixed, a few distinct experimental methods are in practice as described below in Table 1.

Name of the method	Wavelength λ	Diffraction angle θ
Laue method	Variable	Fixed
Rotating-crystal method	Fixed	Variable
Powder method	Fixed	Variable

Table 1: Different types of Xray Diffraction Methods

The average crystallite sizes were calculated using the Debye-Scherrer formula [18] given by the equation (2),

$$\langle D \rangle = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where, β is the FWHM of the Gaussian fit of the diffraction peak, λ is the X-rays wavelength and θ is the Bragg's diffraction angle.

The lattice parameters (a) were calculated by using Miller indices (hkl) values and interplanar spacing with the relation $a = d\sqrt{h^2 + k^2 + l^2}$; where d is the interplanar spacing [19, 20]. The appearance of (220), (311), (400), (422), (511), (440), (620), (533) planes in the diffraction angle assures the formation of cubic spinel structure without any other phase transition. S. Dey et al. [16] found that for $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles the lines in the XRD patterns of samples sintered at temperatures $T \leq 773\text{K}$, are not very sharp as is expected for nanocrystalline materials. The average crystallite size of these samples were found to be less than 10 nm and the average particle size (nm) (from TEM analysis) ranging from ~13 nm to 65 nm with the sintering temperature from 873K to 1173K respectively.

R. Arulmurugan et al. [17] prepared $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.1-0.5$) nanoparticles with particle sizes as observed from the XRD analysis are ranging from 11.1 nm to 8.8 nm respectively and it was observed that the lattice constant decreases from 8.390 to 8.356 i.e. decreases to a very small extent with increase in the Zn concentration since both Co^{2+} and Zn^{2+} ions have small ionic radii. The morphology of the particles formed was examined by direct observation via High Resolution TEM and morphology of one sample was shown in Figure 2.

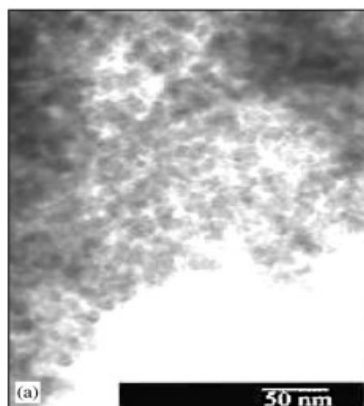


Figure 2: Transmission electron micrograph of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. [R. Arulmurugan et al. Journal of Magnetism and Magnetic Materials vol 288 (2005), 470477]

4. Magnetization Measurements:

S. Dey et al. [16] investigated for $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles, the magnetization measurements (M) versus applied magnetic field (H) were carried out at room temperature (303K) showed that saturation was not reached upto a field 1T. This was expected as it was shown earlier by P.S. Anil Kumar et al. [21] that the magnitude of the magnetic field required to reach saturation depends on the size of the particle. Figure 3 shows that the magnetization values at 1 T (M_{1T}) of the $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ samples with particles sizes <11 nm, decreases with the increasing particle sizes although the trend is usual and also observed in nanocrystalline CuFe_2O_4 and ZnFe_2O_4 materials [22, 23]. Jiang et al. [22] attributed this unusual change in magnetization to spin canting and a drastic change in cation distribution although they suggested that the main contribution for

decrease in magnetization with increasing particle size is due to a change in the cation distribution.

R. Arulmurugan et al. [17] investigated saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) at room temperature in a maximum field of 10kOe. Magnetic properties of Co–Zn ferrites are strongly dependent on the Zn concentration. They found that for the samples $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.1-0.5$), saturation magnetization (M_s) varies from 54.1 emu/g to 39.6 emu/g respectively, for remanence (M_r) it varies from 10.6 emu/g to 0.499 emu/g respectively and for coercivity (H_c) the values are varying from 223 Oe to 9.77 Oe respectively.

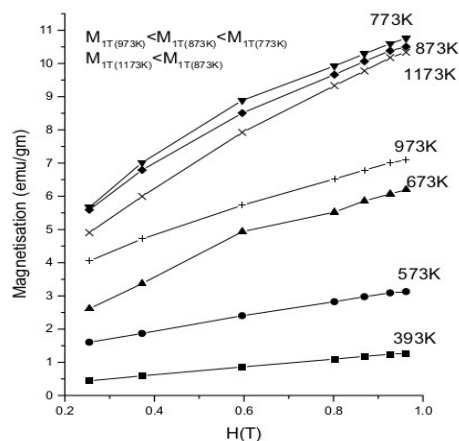


Figure 3: Variation of magnetization with the applied magnetic field of $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ sintered sample. [S. Dey et al., Materials Research Bulletin vol 38 (2003) 1653–1660]

5. Conclusion:

Nanocrystalline $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ and $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.1-0.5$) samples can be prepared by chemical coprecipitation method has a definite impact on the control of particle size and alteration of magnetic properties and with increase in the particle size where cation distribution of $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ changes resulting in a decrease in magnetization with increase in particle size thus magnetic properties of Co-Zn ferrites are strongly dependent of Zn concentration [16,17].

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7. References:

1. J.L. Dormann, D. Fiorani (Eds.), Magnetic Properties of Fine Particles, North-Holland, Amsterdam, (1992).
2. J. Popplewell, L. Sakhnini, "The dependence of the physical and magnetic properties of magnetic fluids on particle size", J. Magn. Magn. Mater. Vol. 149 (issue 1-2), (1995), pp 72-78.
3. K. Raj, B. Moskowitz, R. Casciari, "Advances in ferrofluid technology", J. Magn. Magn. Mater. Vol.149 (issue 1-2), (1995) pp 174-180.

4. U. Hafeli, W. Schutt, J. Teller, M. Zborowski (Eds), Scientific and Clinical Applications of Magnetic Carriers, Plenum Press, New York, (1997).
5. C. Wang, X.M. Zhang, X.F. Qian, J. Xie, W.Z. Wang and Y.T. Qian, "Preparation of nanocrystalline nickel powders through hydrothermal-reduction method", Mater. Res. Bull. Vol. 33(issue 12), (1998) pp 1747-1751.
6. F. Bentivegna, M. Nyvlt, J. Ferre, J.P. Jamet, A. Brun, S. Visnovsky, and R. Urban, "Magnetically textured gamma-Fe₂O₃ nanoparticles in a silica gel matrix: Optical and magneto-optical properties" J. Appl. Phys vol. 85 (Issue 4), (1999) pp 2270-2278.
7. A.E. Berkowitz, R.H. Kodama, S.A. Makhlof, F.T. Parker, F.E. Spada, E.J.Jr. McNiff and S. Foner, "Anomalous properties of magnetic nanoparticles", J. Magn. Magn. Mater. Vol. 196-197, (1999) pp 591-594.
8. J.G.Lee, J. Y. Purk, and C. S. Kim, "Growth of ultra-fine cobalt ferrite particles by a sol-gel method and their magnetic properties", J. Mater. Sci. Vol. 33 (Issue 15), (1998), pp 3965-3968
9. S. N. Okuno, S. Hanshimoto, and K. Inomata, "Preferred crystal orientation of cobalt ferrite thin films induced by ion bombardment during deposition", J. Appl. Phys. Vol. 71 (Issue 12), (1992), pp 5926-5929.
10. F.A. Tourinho, R. Franck, R. Massart, "Aqueous ferrofluids based on manganese and cobalt ferrites", J. Mater. Sci. 25, (1990), pp 3249-3254.
11. R. Massart, V. Cabuil, "Synthesis in an alkaline environment of magnetite colloidal: control of the return and the tail of the particles", J. Chem. Phys. 84 (1987) pp 967-973.
12. J. L. Dormann and M. Nogues, "Magnetic structures in substituted ferrites", J. Phys.: Condens. Matter, Vol. 2, (1990), pp 1123-1237.
13. W. Roos, "Formation of Chemically Coprecipitated Barium Ferrite", J. Am. Ceram. Soc. Vol. 63 (Issue 11-12), (1980) pp 601-603.
14. A. Komarneni, R. Roy, E. Brevel, M. Ollinen, Y. Suwa, "Hydrothermal Route to Ultrafine Powders Utilizing Single and Di-Phasic Gels", Adv. Ceram. Mater. Vol. 1 (1986) pp 87-105.
15. K.J. Davis, K.O. Grady, S. Morup, "The observation of multi-axial anisotropy in ultrafine cobalt ferrite particles used in magnetic fluids", J. Magn. Magn. Mater. Vol. 149(Issue 1-2) (1995) pp 14-18.
16. S. Dey, J. Ghose, "Synthesis, characterisation and magnetic studies on nanocrystalline Co_{0.2}Zn_{0.8}Fe₂O₄", Materials Research Bulletin Vol. 38 (2003) pp 1653-1660.
17. R. Arulmurugan, B. Jeyadevan, G.Vaidyanathan, S. Sendhilnathan, Effect of zinc substitution on Co-Zn and Mn-Zn ferrite nanoparticles prepared by co-precipitation", Journal of Magnetism and Magnetic Materials Vol. 288 (2005), pp 470-477
18. B.D.Cullity, Elements of X-ray Diffraction, 2nd Edn. (Addison Wesley Press. London, (1978).
19. I. Sharifi, H. Shokrollahi, M. M. Doroodmand and R. Safi, "Magnetic and structural studies on CoFe₂O₄ nanoparticles synthesized by co-precipitation, normal micelles and reverse micelles methods" Journal of Magnetism and Magnetic Materials Vol. 324 (2012) pp 1854-1861.
20. R.C. Kambale, P.A. Shaikh, C.H. Bhosale, K.Y. Rajpure and Y.D. Kolekar, "Dielectric properties and complex impedance spectroscopy studies of mixed Ni-Co ferrites". Smart Mater. Struct. 18 (2009) 085014 (6pp)
21. P.S. Anil Kumar, J.J. Shrotri, S.D. Kulkarni, C.E. Deshpande, S.K. Date, "Low temperature synthesis of Ni_{0.8}Zn_{0.2}Fe₂O₄ powder and its characterization", Materials Letters 27 (1996) pp 293-296.
22. J.Z. Jiang, G.F. Goya, H.R. Rechenberg, "Magnetic properties of nanostructured CuFe₂O₄", J. Phys. Condens. Matter. Vol. 11 (1999) pp 4063-4078.
23. H. H. Hamdeh, J. C. Ho, S. A. Oliver, R. J. Willey, G. Oliveri et al. "Magnetic properties of partially-inverted zinc ferrite aerogel powders", J. Appl. Phys. Vol. 81 (4), (1997), pp 1851-1857.