



A REVIEW ON SPINEL FERRITE NANOPARTICLES AND DIFFERENT ASPECTS

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ABSTRACT

A brief introduction to properties and the method of preparation of spinel ferrite nanoparticles have been reviewed. There are different types of mixed ferrite nanoparticles with a number of combinations in the A and B sublattices. Works on mixed ferrite nanoparticles as reported by the different authors have been reviewed.

KEY WORDS: Magnetic properties, Spinel ferrite nanoparticles, Mixed ferrite nanoparticles, Mössbauer spectroscopy.

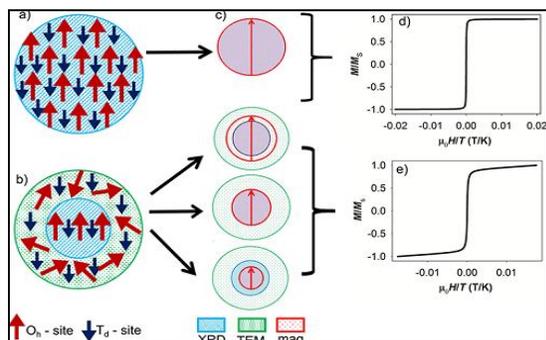
1. REVIEW ON SPINEL FERRITE:

1.1 Spinel ferrite nanoparticles: The main features of magnetic nanoparticles are investigated as fine particles exhibiting properties, which are drastically different from the bulk counterpart [1-6]. This opens up an area of research that is very challenging scientifically and technologically. Fine particles have been widely used for magnetic recording media, ferrofluids, catalysts, electronics, medical diagnostics, drug delivery systems and pigments in paints and ceramics [7, 8-11]. Enhanced magnetic properties of fine ferromagnetic or ferrimagnetic particles make them very promising candidates for high-density magnetic recording media [12].

A large number of techniques have been used to prepare magnetic fine particles including chemical reduction [13], hydrothermal [14], sputtering [15], solvated metallic atom deposition (SMAD) [16], gas evaporation [17], and aerosol synthesis etc. Evaporated fine Fe particles (~ 20 nm) have been reported to have coercivities up to two orders of magnitude higher than the bulk Fe and their saturation magnetization varied from 20-90% of the bulk value depending on the particle size [18]. Particles in the fine form (a few tens of nm) are pyrophoric and hence required a controlled surface passivation. The magnetic properties of the particles are strongly dependent on the form and the constituents of the surface layers, which constitute

a major volume fraction in ultrafine particles. Thus a greater understanding and control of the surface layer would result in optimum magnetic properties.

Reduced magnetization in small ferrite particles is well documented in the literature, but the nature of the spin structure in such particles has not been well understood. Spin canting in ball-milled NiFe_2O_4 [19-20], chemically co-precipitated $\gamma\text{-Fe}_2\text{O}_3$ [21], and acicular $\gamma\text{-Fe}_2\text{O}_3$ recording media particles [22-23] has been



demonstrated via Mössbauer spectroscopy, as a mechanism for moment reduction.

A principal effect of finite size on a magnetic particle is the breaking of a large number of exchange bonds for surface atoms. This can have a particularly strong effect on ionic materials, since the exchange interactions are largely antiferromagnetic, superexchange [24-25] interactions. This interaction is an indirect exchange mechanism whereby electrons are shared between 3d orbitals of the metal ions and 2p orbitals of oxygen ions. The interaction strength is proportional to the overlap between these orbitals; hence it depends on the bond length and angle between the metal ions and the intervening oxygen ion. When some exchange bonds are removed at the surface, there can be frustration and spin disorder [26-28].

The magnetic properties of a spinel ferrite are strongly dependent on the distribution of the different cations among tetrahedral (A) and octahedral (B) sites in the crystal lattice. The cation distribution in magnesium ferrite has been studied by various authors and was found to be strongly temperature dependent [29-32]. Magnesium ferrite requires high sintering temperatures of the order of 1350 °C to achieve the desired control on the Mg^{2+} ions distribution on octahedral and tetrahedral sites [33]. The cation distribution of slowly cooled magnesium ferrite was reported by Blasse [34] as $(Mg_{0.1}^{2+}Fe_{0.9}^{3+})^A(Mg_{0.9}^{2+}Fe_{0.1}^{3+})^B O_4^{2-}$. Most of Mg^{2+} ions are located on B-sites and a small fraction migrates to A-sites.

1.2 Mixed ferrites nanoparticles: There are different types of mixed ferrite nanoparticles with a number of combinations in the A and B sublattices. Following is a brief review of some of the works on mixed ferrite nanoparticles as reported by different authors.

Nobuyuki Kikukawa et al. [35] prepared zinc-substituted spinel ferrite fine particles of $M_{1-x}Zn_xFe_2O_4$ (M=Mg, Mn, Co, Ni, Cu, (Li, Fe) $x=0-1$) with good crystallinity and stoichiometry using a glycine-nitrate process. The product powder was an agglomerate of fine particles whose typical diameter were several tens of nanometers. X-ray diffraction patterns revealed that the produced particles were mono-phase in almost all reaction systems. Energy-dispersive x-ray spectroscopy microanalysis of the product particles (Mn-Zn-Fe-O) revealed that the distributions of Mn/Fe ratio and Zn/Fe ratio were highly sharp both within the agglomerate and between agglomerates.

Nanoparticles of $Ni_{0.25}Co_{0.25}Zn_{0.5}Fe_2O_4$ with different particle sizes were synthesized by the chemical co-precipitation technique by Omprakash Suwalka et al. [36]. The prepared nanoparticles were characterized and studied by X-ray diffraction, room temperature ^{57}Fe Mössbauer spectroscopy and DC magnetization. Increase in annealing temperature leads to inversion of cations from their normal configurations which results in an increase in the hyperfine fields at both tetrahedral A and octahedral B sites. The decrease in saturation magnetization values with an increase in annealing temperature can be attributed to the variation in proportions of superparamagnetic phase and also the redistribution of cations in these ferrite nanoparticles. Variation of coercivity with annealing temperatures can be explained in terms of the size effect.

Ni-Cu-Zn ferrites have been synthesized by employing the co-precipitation technique using oxalate precursors by S.A. Ghodake et al. [37]. X-ray diffractograms did not show impurity phases, indicating single-phase formation of the ferrites. The diffractograms of oxalate complex decomposed at 650 °C show that ferritization is complete at 650 °C. Lattice parameter a (Å) was found to decrease with the addition of Ni^{2+} which is attributed to ionic sizes of Ni^{2+} (0.69 Å), which replaces Cu^{2+} (0.72 Å). Initial permeability (μ_i) shows increase when Ni^{2+} is added up to $x=0.15$ while for $x>0.15$, it decreases. The increase in initial permeability (μ_i) is attributed to monotonic increase in M_s , and crystalline magnetic anisotropy constant (K_1) on addition of Ni^{2+} . However, the microstructure and density (porosity) also influence μ_i variations. The decrease in μ_i is attributable to increase of K_1 . The composition with density 91.14% exhibits large μ_i , which also tends to increase with temperature up to 60 °C. Thus its usable range extends up to 60 °C. This samples has T_c near to 160 °C.

The effect of copper substitution on microstructure and composition related magnetic properties in a series of nominal composition $Ni_{(0.8-x)}Zn_{0.2}Cu_xFe_2O_4$ (where, $x=0, 0.05, 0.10, 0.15, 0.25, 0.42, 0.45, 0.5, 0.55$ and 0.6) samples were investigated by I.Z. Rahman et al. [38]. XRD patterns of powder samples showed the cubic spinel phase up to $x=0.25$ and a second phase of composition CuO above $x>0.25$. The crystallite sizes of as-dried samples when calcined at high temperatures changed from ~ 10 to ~ 50 nm at 1000°C . The partial substitution of Ni^{2+} with divalent cations Cu^{2+} influenced the magnetic parameters due to modification by cation distribution.

Ultrafine $Co_{1-x}Zn_xFe_2O_4$ ($0 \leq x \leq 1.0$) particles prepared by a sol-gel method by Seung Wha Lee et al. [39] and the magnetic and structural properties of the powders were investigated with x-ray diffraction, vibrating samples magnetometer and Mössbauer spectroscopy. The lattice parameter (a_0) increases linearly with increasing Zn concentration (x) and follows Vegard's law approximately. Mössbauer spectra of Co-Zn ferrite have been taken at various temperatures from 20 to 800 K. The isomer shifts indicate that the iron ions were ferric at the tetrahedral (A) and the octahedral (B) sites.

Nanocrystalline $Co_{0.2}Zn_{0.8}Fe_2O_4$ has been synthesized by the co-precipitation method by S. Dey et al. [40]. XRD shows that the spinel ferrite is formed after sintering the sample at 393 K. Nanoparticles with average particle size of 5–65 nm were obtained by sintering the samples between 393 and 1173 K. FTIR show that spinel ferrites prepared by the co-precipitation method retain some hydroxyl groups, which are not removed completely by sintering at temperatures ≤ 873 K. DTA/TG measurements show that between 573 and 823 K spinel is formed and a small weight loss above 873 K is due to removal of hydroxyl. Saturation magnetization of the samples increase with increasing average particle size upto 11 nm and for samples with particle size >11 nm, the saturation magnetization decreases with increasing particle size. This is due to a change in cation distribution with change in particle size.

1.3 SUMMARY OF REVIEWS AND CONCLUSION:

The above review thoroughly discusses the different aspects of spinel ferrite and mixed ferrite nanoparticles. The methods of preparation of ferrite nanoparticles were discussed. The structural and magnetic properties of different types of mixed ferrite nanoparticles have been reviewed. The magnetic properties of the particles are strongly dependent on the form and the constituents of the surface layers in nanoparticles. Thus a greater understanding and control of the surface layer would result in optimum magnetic properties.

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