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Preparation of magnetite nanoparticles and interpreting their magnetic behavior in wetting

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Abstract:

The wet chemical route of co-precipitation method is used to synthesize ultrafine magnetite for study. Using XRD, the estimated average size was ~24nm and confirmed the phase Fe_3O_4 with inverse spinal structure. The M-H loop of the Fe_3O_4 has investigated the magnetic entities and has confirmed the single domain nature. The paper has reported the magnetization saturation of Iron Oxide nanoparticles (IONs) increases with wetting. The effect of wetting has been discussed from the theoretical point of view. Dependency of magnetic property on the K, a and size for an effect was considerably analyzed in this study.

Keywords: Magnetic Nanoparticles, Fe_3O_4, Wetting effect, SPIONs, Iron Oxide, Coprecipitation.

INTRODUCTION

MNP (magnetic nanoparticles) shows the good heating effect, depending on the frequency and magnitude of magnetic field and the size, shape and permeability of MNP [1]. This can be used for the treatment of the cancer simultaneously with chemotherapy. Amit Sharma and his team studied MNP for cancer treatment and showed that IONs are nontoxic [2]. MNP can be used for drug delivery after coating and attaching drug to it [3]. Thus this requires the MNP with less but not zero coercivity H_c, high saturation magnetization (M_s) and probably a low remanence ratio [1][2][4][5]. The particles with size 20 – 30 nm are considered as single domain structure. As a size decreases, superparamagnetic Iron Oxide nanoparticles (SPION) are obtained which can play crucial role in drug delivery. The magnetic behavior changes and tends to vanish for very small size, above which a relaxation in H_c occurs. During above mentioned applications, these particles are wetted and dispersed. Therefore, what is the effect on magnetic properties of magnetite needs to be studied. In this regard water is proposed as a wetting medium. And for the magnetite phase spinel structure of the Iron Oxide was selected. Interest of investigation is what happens if the MNP are just wetted and fully wetted or just dispersed. Therefore, this paper is investigating the Iron Oxide Nanoparticles size with their magnetic behavior from a M-H loop and the effect of wetting on it.

EXPERIMENT

Magnetite was synthesized by the wet chemical route of co-precipitation method. Magnetite ultrafine particles were prepared at 300K, without surfactants. The Ferric Chloride Hexahydrated, ($FeCl_3.6H_2O$) and Ferrous Sulfate Hydrated ($FeSO_4.7H_2O$) in a proportion of 2:1 in deionized double distilled water and ammonia solution were used as source chemicals. Only the A.R. grade chemicals were used without post-purification. The X-ray diffraction (XRD) was carried out on a Philips X-Ray Diffractometer using Cu-Kα radiation of wavelength (λ) approximately 1.540Å with step size 0.02. The PC based pulsed M-H loop tracer system with the range of field between -6KOe to 6 KOe was used for magnetic study at room temperature. The room temperature was maintained 20^oC.

RESULT AND DISCUSSION

In X-ray diffraction, data plotted in Fig.1, all the peaks (possibly convoluted) corresponding to Iron Oxide were observed by comparing the reported work in literature. The peaks are close to those reported by D. Maitly, D.C. Agrawal [4] for ratio 2:1 of Fe^{3+} to Fe^{2+}. Their relative Intensity matched with a Phase Magnetite i.e. Fe_3O_4. These peaks show cubic structure. Indexing of profile gave 2θ=35.6 for 100% intensity, miller indices (311) and other prominent peaks at 2θ 30.14, , 43.16, 53.68, 57.14, 62.66 for miller indices (220), (400), (422), (511), (440) respectively. The absence of sharp peaks and presence of broadened peaks indicates the presence of nanosize grains [6]. The Lattice parameter is determined using following relation [7]:

$$F(\theta) = \frac{1}{2}\left[\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right] \qquad (1)$$

Where, θ is Bragg’s angle and bracket term is called the Nelson-Riley function [6]. Lattice parameters were calculated for each angle using the equation (2)

$$a = \frac{\lambda^2}{4\sin^2\theta} \times (h^2 + k^2 + l^2) \qquad (2)$$

A graph was plotted “a” as a function of $F(\theta)$. The precise value of “a” was obtained by extrapolating straight line with fitting as shown in Fig.2. Found value in four significant figure of “a” is 8.373 with an error 0.0145$\AA$ and volume of the unit cell is obtained 586.96 nm^3. From this density found 5.24gm/cm^3. The graphical visualization data of a refined unit cell has been drawn using the VESTA program [8] (illustrated in Fig.3). For both choices of structure in the form of polyhedrons (blue for octahedral and green for tetrahedral) made by Oxygen atoms are shown and Fe-atoms at its center in red and brown colors.

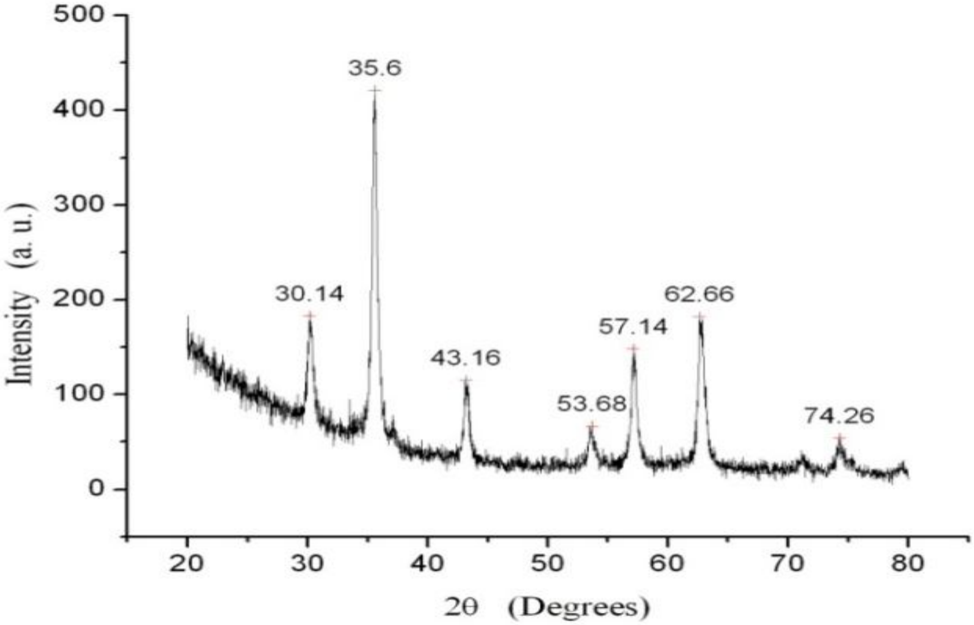

Figure 1: Shows X ray diffraction of IONs

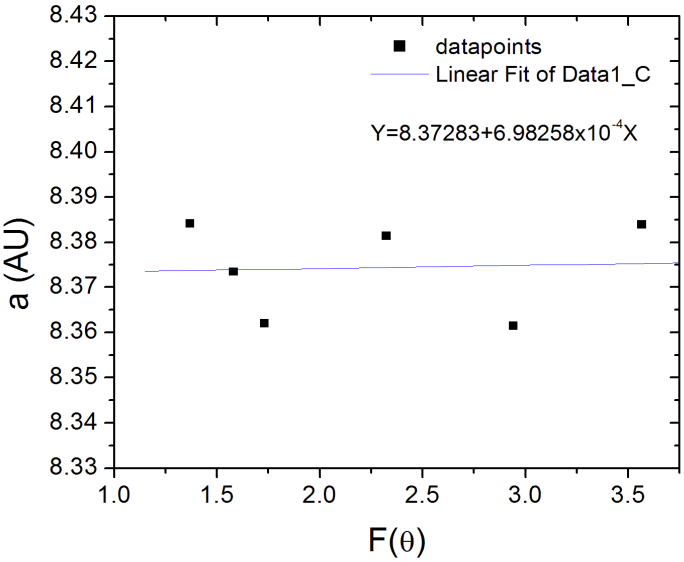

Figure 2: Finding Lattice parameter

Broadening of peaks (calculated after broadening correction) measured by β_{hkl} (Full Width of Half Maxima) increases with the angles of diffraction illustrated in inset of Fig.4 with the help of fitting curves. It has suggested the single domain structure. In the present work, the same procedure is used to calculate the crystalline size and strain in the powder sample as discussed by VD Mote et. al. [9]. Fig.4 shows the William Hall plot from which the strain is calculated as 0.0041 with error 0.0014 and the size of particles is estimated from the intercept of linear fitting on y-axis $\beta_{hkl}\cos\theta$ at the origin of x-axis $4\sin\theta$ i.e. 0.00568. The average size of crystalline particles is found 24.40±2.8nm. The estimated average size has suggested that the single domain structure or below its size, i.e. diminishing with the occurrence of superparamagnetism.

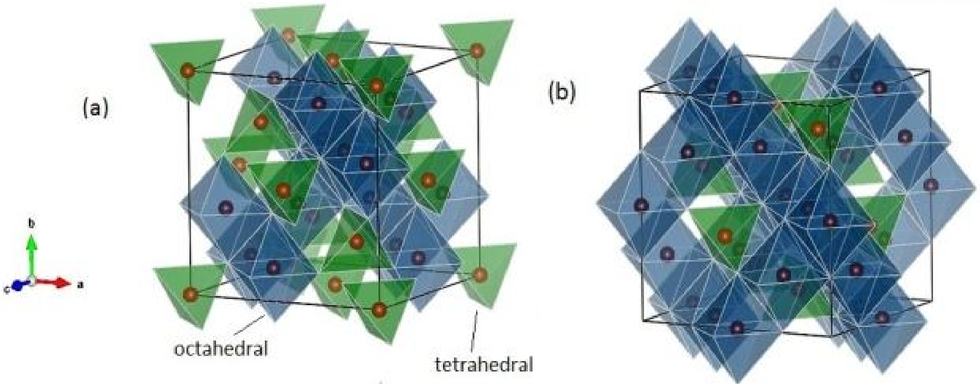

Figure 3: TheUnit cell of magnetite lattice choices for the Fd3m cubic structure- (a) choice 1 and (b) choice 2. In both, red balls are tetrahedrons placed in green tetrahedral and brown balls are octahedron in blue octahedral. Corners of polyhedral represent Oxygen atoms.

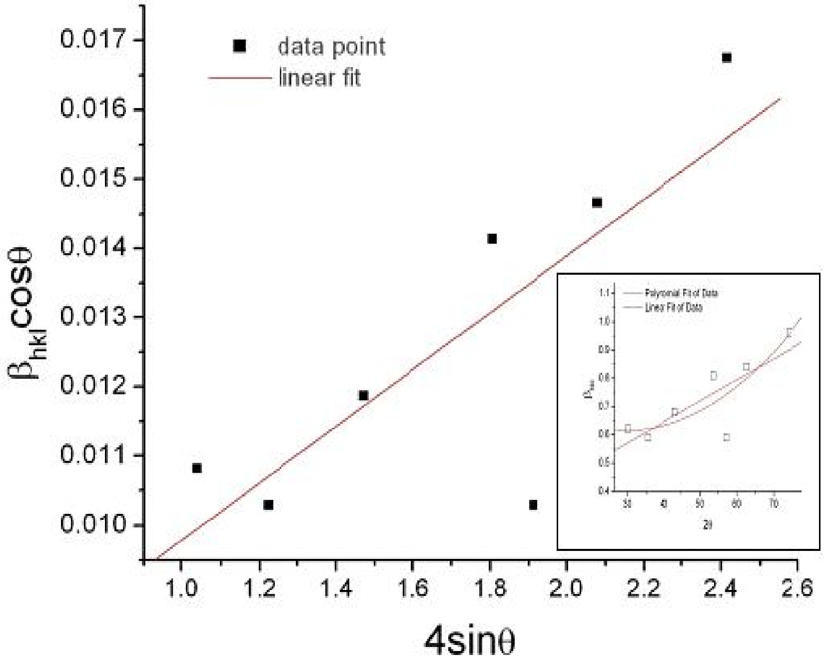

Figure 4: Williamson-Hall plot for size and strain analysis

The Magnetic properties are traced out by M-H hysteresis as illustrated in Fig.5. For the powder of Fe_3O_4, 95.81Oe coactivity (H_c) with magnetization saturation (Ms) of 64.40 emu/gm has been found which indicates the existence of the single domain structure. Shortly, the superparamagnetic nature is observed and indicated the just formation of SPION. Also magnetization saturation achieved for small (above 1KOe) field strength H with H_c = 95.81emu/gm. These features render these IONs in the area of biomedical for various applications, particularly for the drug delivery and for the hyperthermia treatment to cure cancer [1] [2] and [5]. The remanence ratio M_r/M_s is smaller than that of the value of single-domain particles 0.5 expected for noninteracting, randomly oriented [5].

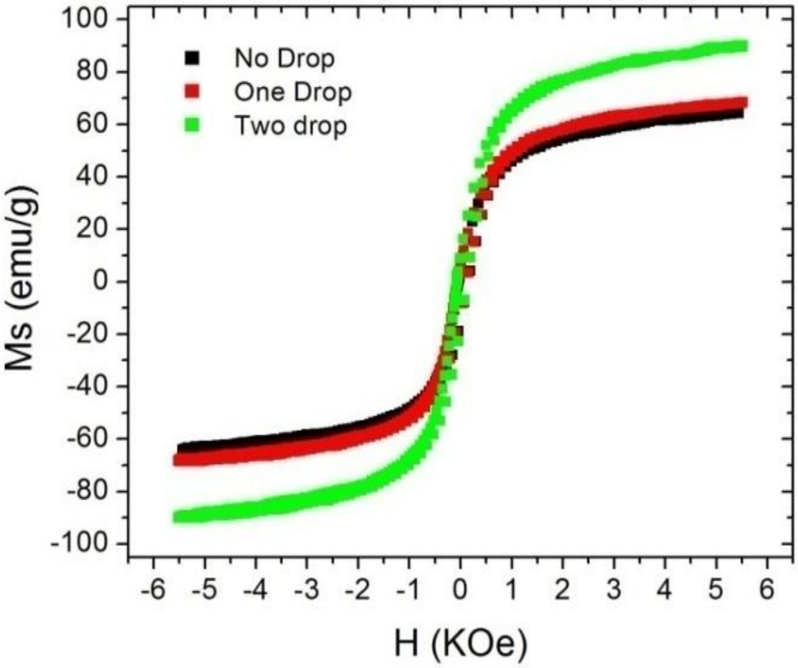

Figure 5: M vs. H curve of Fe3O4 with i)no drop, ii) one drop, iii) two drops of addition of distilled water (H2O) for wetting.

Table 1: Parameters shows Wetting effect on IONs:

Drop of H_2O	H_c (Oe)	M_r (emu/gm)	M_s (emu/gm)	Remanance ratio
No	95.81	14.65	64.40	0.227484
One	87.43	9.41	68.54	0.137292
Two	95.38	14.80	90.20	0.16408

The wetting effect of magnetite in the deionized water (H_2O) is illustrated in Fig.5. Comparisons of some parameters are given in a Table1. It shows an increment in M_s with the addition of a drop of H_2O. But the magnetization of saturation started at field strength is almost similar (~ 1KOe) for all three loops. A variation in M_s due to the addition of drop shown that the changes occur in susceptibility. However the wetting affects remanence ratio to increase for the deionized water for the first drop and then decreases for the second drop. This shows particles are becoming free from interaction with each other and randomly orienting. Possibly the domain structure is vanishing. This may be due to the dissociation of agglomerated particles that begin with increasing drops. One other thing that seems interesting is the increment in slope at the H_c of the curve of hysteresis.

This has clearly indicated the vanishing of present magnetic crystalline anisotropy of a wet magnetite. Thus and due to its itself plot of fitting of many data-points, we preferred to take this slope countable instead squareness factor or remanence ratio for the wetting effect on below the single domain ultrafine particles of magnetite. In the presence of water medium magnetite particles may make themselves free to switch easily to their easy axis and hence possibly slope at H_c increases as well as remanence ratio decreases. It may become more and more non-interacting. Such particles are randomly oriented at an ambient room temperature.

The variation of H_c with the particle size can be explainable on the basis of domain structure, critical size, and the surface and interface anisotropy of a crystal. A crystallite will spontaneously break up into a number of domains in order to reduce the large magnetization energy if it is a single domain. The critical size from a single domain to multidomains can be calculated [10] by using spherical particle model formula (see equation (3)):

$$D_m = \frac{9\sigma_\omega}{2\pi M_S^2} \qquad (3)$$

Where $\sigma_\omega = \sqrt{2k_B T_C |K_1| / a}$ is a domain wall energy, k_B is Boltzmann constant, T_C Curie temperature, $K_1$is magnetocrystalline anisotropy constant, 'a' is lattice parameter and M_s is saturation magnetization. Below D_m particle remain single domain and above became multidomains. Theoretically, this value is approximately close to 30nm at room temperature. If the size is below D_m then M_s decreases. This is applicable to our case. For the same sample Dm is constant and therefore the equation (4).

$$\frac{\left|\sqrt{|K_2|/a}\right|_2}{\left|\sqrt{|K_1|/a}\right|_1} = \frac{M_{S2}^2}{M_{S1}^2} \qquad (4)$$

In our sample, the XRD estimated particle size D=24.40nm has confirmed a single domain. These discussions pointed to that a 'σ_ω' should not be a constant and smaller variation in $\boldsymbol{K_1}$ *and* $\boldsymbol{a}$ quantities may occur.

Let us consider the 'a' is remaining constant throughout wetting then only 'K' would vary according to the M_s. This indicate shape and size changes are dominating. Wetting may cause some changing in it and also it may release strain. In XRD, shapes of the peaks are observed symmetric to its center. The pseudo-Voigt function fitting of XRD data agreed to have symmetry in shape of the peak profile. This indicated that the grain-particles preferentially spherical in shape. Now a change in 'K' is mostly due to size. But smaller experimental values of H_c indicated it must then be very small but significant.

Let us consider 'a' is not constant and the shape is spherical. Then the above equation didn't give a satisfactory value of "a" and suggested the significance of 'K'. Along with it, we are focusing on the equation$M_s a^3 = N_{\mu_B}\mu_B$, where M_s is saturation magnetization per gram N_{μ_B} is the numbers of Bohr magnetons per unit cell (32 in magnetite) and μ_B is Bohr Magneton (=9.27×10^{-27} in SI) [11]. By considering $N_{\mu_B}\mu_B$ is constant for the magnetite got $M_s a^3 = Constant$. This equation indicated that, for the same species Saturation magnetization depends on the volume of a unit cell.

Either impossible in a change in N_{μ_B} for standard magnetite is suspicious or the shape, size of particle grain must have taken part in changing Ms as seen in the previous discussion. Thus, if the increase in Ms by wetting significantly introduced the very small change in the unit cell edges, then for very small change it was varying 8.37, 8.201 and 7.483 in Å for no wet, a one-drop and a two-drop wet respectively. Other two 'a's are smaller than the expected for the phase of magnetite. Up to what extend variation in 'a' were examined using the 0007418-to-24 AMCSD [12] database for the higher pressure. It shows 'a' does not approach to our later estimated values. For a single domain, the confirmation of the nature of H_c data for expected size can be figured out by equation (5)

$$H_c = g - \frac{h}{D^{3/2}} \qquad (5)$$

Where g and h are constants. This indicates diameter of the grain-particle increased slightly for the addition of first drop and then come back nearer to the previous size on the addition of second drop. First two sizes were tally with increasing value of M_s but last one didn't. This has suggested that instated of size of particles the modification of shape was dominating for the second drop. Now smaller H_c, M_r in Table1 for one drop can be justified, that however the volume of unit cell and volume of nanoparticles reduces due to an assumed contraction, the wetness give medium to orient the moments more easily to their easy axes as well as bounded particles to free and attributed their moments to increase saturation magnetization. Second drop possibly gives enough freedom for dispersion so that maximum free particles are available to contribute in increase of M_s.

CONCLUSION

The change in particle size due to wetting has been revealed. Wetting effect indicates increase in M_s and decrease in remanence ratio and increases slope at H_c for a cold drop. Therefore the consideration of the size of grain-particles, magneto crystalline anisotropy and lattice parameter are necessary.

(1) Random orientations of the particle are found. (2) Few of Fe atoms at the edges in unit cell on the free surface of each grain-particles interacted with others. (3) This makes some of them cancel the moment due to random orientedness in forming or in a bigger grain-particle. (4) In wetting some of the grain-particles got freedom and showed full moment. (5) Until all grain-particles got separated from each other, the Ms seem increased and then remain unchanged thereafter. (6) Partly separation process could have influenced the shape and therefore the change in shape dependent anisotropy directed to change in Hc during just wetting.

The magnetic behavior suggested that this Magnetite is probably the ideal candidate for hyperthermia treatment for cancer and drug delivery and this study suggested that the requirement of more hydration in a body of a subject.

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CORRIGENDUM

We regret to inform that the paper entitled “**Surface Tension of Sn-Ag and Sn-Zn Binary Liquid Alloy**” Published in the Bulletin of Pure and Applied Sciences Vol. 33 D(Physics) Issue (No. 1-2) 2014: p.29-32 was co-authored by kuimari Archana, Research Scholar and Om Prakash Roy, Department of Physics, B.R.A. Bihar University, Muzaffarpur (Bihar).

Hence, the paper as referred to above may kindly be read as:

“Surface Tension of Sn-Ag and Sn-Zn Binary Liquid Alloy” Kumari Archana, Research Scholar and Om Prakash Roy, Department of Physics, B.R.A. Bihar University, Muzaffarpur (Bihar).

on the **title page(29)** of the paper in the journal and the **Contents** as well.

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