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Supplementary Information for

Influence of spherical assembly of copper ferrite nanoparticles on magnetic properties: Orientation of magnetic easy axis

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Atomic Absorption Spectroscopy (AAS) analysis

Atomic absorption spectroscopy analysis (AAS) of the ionic solution of the NP and NS samples were carried out to determine the concentration of metal ions and consequently the chemical composition of the respective samples.

Initially, a pinch of sample was added to 10 ml of conc. HCl solution and kept in a ultrasonicator for 1 h to ensure the complete dissolution of the particles. Then, 300 µl of the as-prepared solution was added to 30 ml of deionized water in a volumetric flask to prepare a diluted stock solution of the constituting metal ions (Cu^{2+}, Fe^{3+}). The diluted stock solution was then used for the AAS analysis and the results are contained in **Table 1**.

Table 1: Atomic Absorption Spectroscopy (AAS) data

Standard samples							
Standard concentration of Cu^{+2} ions				Standard concentration of Fe^{+3} ions			
1 M, 3 M, 5M				2 M, 4 M, 6M			
Sample Information (0.3 ml×S_1 = 30 ml×S_2)							
NP				**NS**			
Cu^{+2} conc. (S_2) (ppm)		Fe^{+3} conc. (S_2) (ppm)		Cu^{+2} conc. (S_2) (ppm)		Fe^{+3} conc. (S_2) (ppm)	
0.0168		0.0294		0.0129		0.0316	
0.0156	0.0165	0.0301	0.0292	0.0144	0.0137	0.0304	0.0308
0.0171		0.0281		0.0138		0.0307	

From the value of S_2, the value of S_1 is calculated for NP and NS samples as given by

For NP sample,	For NS sample,
S_1 of copper = 2.604×10^{-5} M,	S_1 of copper = 2.162×10^{-5} M,
S_1 of iron = 5.234×10^{-5} M.	S_1 of iron = 5.516×10^{-5} M.

Therefore, the molar ratio of the metal ion (Cu : Fe) present in NP sample = 2.604 : 5.234,

i.e., 0.4975 : 1

And the molar ratio of the metal ions (Cu : Fe) present in NS sample = 2.162 : 5.516

i.e., 0.392 : 1

From the ratio of metal ions in the respective samples, the chemical composition of the samples can be estimated. The most accurate composition of the NP sample would be: Cu(0.995) : Fe(2).

And the composition of NS sample would be: Cu(0.784) : Fe(2).

Therefore, the composition of one unit formula of the NP sample should be: $Cu_{0.995}Fe_2O_4$.

And the composition of one unit formula of the NS sample should be: $Cu_{0.784}Fe_2O_4$.

X-ray Diffraction analysis

In case of cubic crystal, the lattice constant (a), can be calculated using the following relation[1]

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad (1)$$

By plotting the value of ($h^2 + k^2 + l^2$) versus $1/d_{hkl}^2$, the lattice constant (a) was determined to be 8.4031 Å and 8.3745 Å for NP and NS sample respectively.

The mean interionic distances in tetrahedral (A) and octahedral (B) crystallographic sites and mean site radii in cubic spinel (AB_2O_4) structure are function of lattice parameter (a) and oxygen positional parameter (u). The cation-anion bond length in A site (R_{OA}), and B site (R_{OB}), tetrahedral edge (d_{AE}), shared and unshared octahedral edges (d_{BE} and d_{BEU} respectively), mean A site radius (r_A) and mean B site radius (r_B) for NP and NS samples are calculated using the Reitveld refined parameters (u and a) according to the following equations[2]

$$R_{OA} = a\sqrt{3}(u - 0.25) \quad (2)$$

$$R_{OB} = a\left(\frac{5}{8} - u\right) \quad (3)$$

$$d_{AE} = a\sqrt{2}(2u - 0.5) \quad (4)$$

$$d_{BE} = a\sqrt{2}(1 - 2u) \quad (5)$$

$$d_{BEU} = a\left(4u^2 - 3u + \frac{11}{16}\right)^{\frac{1}{2}} \quad (6)$$

$$r_A = a\sqrt{3}(u - 0.25) - R_o \quad (7)$$

$$r_B = a\left(\frac{5}{8} - u\right) - R_o \quad (8)$$

Here u is defined with the unit cell origin at an A site and R_o is the ionic radius of oxygen (1.32 Å).

For the $CuFe_2O_4$ system under investigation, the distribution of the cations over the tetrahedral (A) and octahedral (B) sites can be expressed in terms of the degree of inversion (x) as

$$(Cu^{+2}_{x}Fe^{+3}_{1-x})^{A}\,[Cu^{+2}_{1-x}Fe^{+3}_{1+x}]^{B}$$

Therefore, the mean radius of the ions at the tetrahedral and octahedral site respectively are given by

$$r_A = x\, r_{Cu^{+2}} + (1 - x)\, r_{Fe^{+2}} \quad (9)$$

$$r_B = \frac{1}{2}[(1 - x) r_{Cu^{+2}} + (1 + x)\, r_{Fe^{+2}})] \quad (10)$$

On the other hand, the mean radius of the ions at the tetrahedral and octahedral sites is given by equation 6 and 7. Using the value of oxygen ionic radius ($R_o = 1.32$ Å), Rietveld refined values of a and u, and solving equations (6 to 9), x can be determined and therefore, the cation distribution can be estimated. The estimated cation distribution for NP sample is given by

$$(\mathrm{Cu}^{2+}{}_{0.08}\,\mathrm{Fe}^{3+}{}_{0.92})^{A}\,[\mathrm{Cu}^{2+}{}_{0.92}\,\mathrm{Fe}^{3+}{}_{1.08}]^{B}$$

Magnetic property analysis

Orientation of magnetic easy axis:

Considering FC magnetization at low temperature ($T \rightarrow 0$), it is possible to verify the degree of alignment of the magnetic easy axis in a nanocrystals assembly. At a temperature much lower than the mean blocking temperature (T_B), FC magnetization can be described by[3]

$$M_{FC} = \langle \cos^2\beta \rangle \frac{M_S^2(0)}{K_E} \ln\left(\frac{\tau_w}{\tau_0}\right) n(V)VH \tag{11}$$

where β is the average angle between easy magnetic axis and applied magnetic field, $n(V)$ is the volume distribution function, τ_o is a characteristic relaxation time and τ_w is the experimental time scale. For a sample with random distribution of easy axis $<\cos^2\beta> = 1/3$ and the equation (10) can be rewritten:

$$M_{FC} = \frac{M_S^2(0)}{3K_E} \ln\left(\frac{\tau_w}{\tau_0}\right) n(V)VH \tag{12}$$

If a sample is characterized by a partial orientation of easy axis, and by assuming a fraction α and (1-α) of nanoparticles having aligned and random easy axis respectively, the FC magnetization can be written as:

$$M_{FC}^{align} = \frac{M_S^2(0)}{3K_E} \ln\left(\frac{\tau_w}{\tau_0}\right) n(V)VH(1 - \alpha + 3\alpha\cos^2\beta) \qquad (13)$$

The ratio M_{FC}^{align}/M_{FC} can be written as

$$M_{FC}^{align}/M_{FC} = 1 + \alpha(3\cos^2\beta - 1) \qquad (14)$$

If all the particles are randomly oriented, $\alpha = 0$ and $M_{FC}^{align} / M_{FC} = 1$, while the presence of a fraction of particles with oriented easy axes leads to $M_{FC}^{align} / M_{FC} \neq 1$.

References

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