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Co-Precipitation Synthesis, Optical and Magnetic Properties of $Mn_xFe_{1-x}Fe_2O_4$ Ferrofluids

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Abstract: Manganese substituted ferrite ferrofluids were synthesized via chemical co-precipitation techniques using metallic chlorides of manganese and iron in alkaline pH. The structural investigation of the prepared samples was performed with x-ray diffractometer (XRD), which showed broadening of the diffraction peaks. Magnetic properties were studied by vibrating sample magnetometry (VSM) at room temperature. VSM results were consistent with the expected theoretical magnetization values for the composition of magnetite particles. Study of refractive indices using High Resolution Spectrometer shows refractive indices increased up to a certain limit and attained saturation. Polarimeter readings show that the field increases the angle of rotation also increases, up to a certain limit and after that it appeared to be a constant.

Introduction

Ferrofluids are colloidal liquids made of nanoscale ferromagnetic or ferrimagnetic, particles suspended in a carrier fluid (usually an organic solvent or water)[1]. In ferrofluids, each tiny particle is thoroughly coated with a surfactant to inhibit agglomeration. Large ferromagnetic particles can be cleavaged out of the homogeneous colloidal mixture by forming a separate clump of magnetic nanoparticles when exposed to strong magnetic fields[2]. The surfactant's Van Der Waals force is sufficient to prevent magnetization in the absence of an externally applied field as magnetic attraction of nanoparticles is weak and thus is often classified as"superparamagnets" rather than ferromagnets[3-5].

Ferrofluids are composed of nanoscale particles (diameter usually 10 nanometers or less) of magnetite, ferrites or some other compound containing iron which are stable, preventing agglomeration with gravitational set up. The composition of a typical ferrofluid is about 10% magnetic solids, 5%surfactant and 85%carrier, by volume.

Super paramagnetic manganese ferrite possesses extensive applications in drug targeting and magnetic hyperthermia[6]. The magnetic particles in ferrofluid are generally magnetite; the magnetic properties of magnetite that make it a desirable component of ferrofluids are derived from its crystal structure. Magnetite crystallizes in the inverse spinel structure above 120K.

In this paper, we report the synthesis of manganese substituted magnetite particles by co-precipitation of metallic chlorides of manganese and iron and their structural and magnetic properties are evaluated[8].

Experimental Details

Synthesis of manganese ferrite powder

Manganese ferrite powder is prepared from a homogeneous aqueous solution of $FeCl_3$ and $FeSO_4$ at room temperature. The precipitate is precoated with surfactant, oleic acid and the wet slurry is dried and dispersed in kerosene. In order to get manganese substituted magnetite ferrofluid, the same procedure is using in co-precipitation synthesis of manganese chloride (0.2, 0.4, 0.6, 0.8). A similar procedure is adopted in the case of manganese substituted magnetite ferrofluid($Mn_xFe_{1-x}Fe_2O_4$).

The chemical equation showing the reaction is

$$2\ FeCl_3+(1-x)\ FeSO_4.7H_2O+x\ MnCl_2\ 4H_2O+NH_4.OH.16H_2O=Mn_xFe_{1-x}Fe_2O_4+NH_4Cl \quad (1)$$

Structural Analysis

Manganese substituted ferrite nanoparticles have been analyzed using X-ray diffraction (XRD), (Rigaku Dmax-C X-ray power Diffractometer using Cu $K\alpha$,λ=1.5404A^0 Radiation). Grain size of nanopowder is determined by using Debye-Scherrer formula. Peaks are identified for the samples in the JCPDS data. (JCPDS PDF # 10-0319)

Magnetic Properties

Manganese substituted magnetite nano powders have been analyzed using vibrating sample magnetometer (VSM) for magnetic characterization of different concentrations. Hysteresis loop is traced and parameters namely saturation magnetization (M_s), coercive field (H_c), remanence (M_r) and squareness ratio (M_r/M_s) are evaluated.

Faraday rotation

Faraday rotation is measured by using standard ellipsometer set up. Faraday rotation and ellipticity are magneto optical properties observed in the longitudinal mode in which the direction of propagation of polarized light and the magnetic field are the same. Faraday rotation is the rotation of the plane of polarization of light by the medium in presence of an applied magnetic field.

High resolution spectrometer for refractive indices measurements

Refractive indices in different concentration of $Mn_xFe_{1-x}Fe_2O_4$ ferrofluids were measured by deviation method[7].

The refractive indices calculating using the formula,

$$\mu = \frac{\sin\left(\frac{A+B}{2}\right)}{\sin\left(\frac{A}{2}\right)} \quad (2)$$

Results and Discussion

Structure Analysis:

The formation of $Mn_xFe_{1-x}Fe_2O_4$ particles by co-precipitation of Mn^{2+}, Fe^{2+} and Fe^{3+}in an alkali medium is fairly well known and is widely used for the mass production of ferrofluids. In this investigation, the samples synthesized via co precipitation of metallic salts are analyzed by XRD for their structural characterization, which shows the formation of $Mn_xFe_{1-x}Fe_2O_4$ particles with traces of hematite as the impurity. Hematite, the non magnetic form of iron oxide is one among the major impurity that is generally formed during the synthesis of ferrofluids. However, by careful optimization of the pH, the formation of hematite can be made limited. The XRD peaks can be indexed into the spinel cubic lattice type. It cannot be ascertained from the XRD whether the further oxidized Fe_2O_3 phase exists in the sample because of similar lattice constant. XRD shows broadening of the diffraction peaks due to lower grain size. However, XRD patterns (Fig1a, 1b and 1c) show the presence of pure spinel structure for Manganese substituted magnetite nanofluids. The samples are polycrystalline in nature.

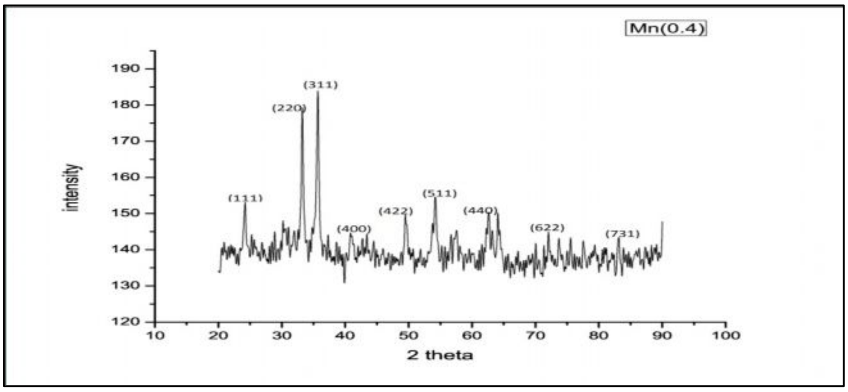


Figure 1(a):Graph obtained from XRD studies on $Mn_{0.4}Fe_{0.6}Fe_2O_4$ nanopowder

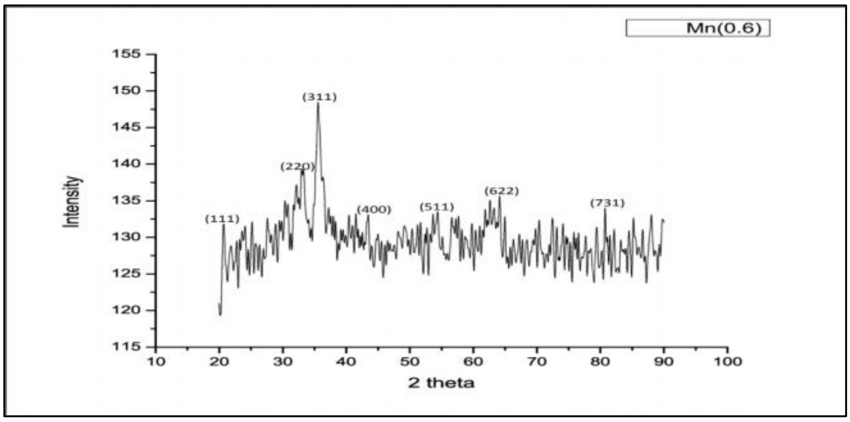


Figure 1(b):Graph obtained from XRD studies on $Mn_{0.6}Fe_{0.4}Fe_2O_4$ nanopowder

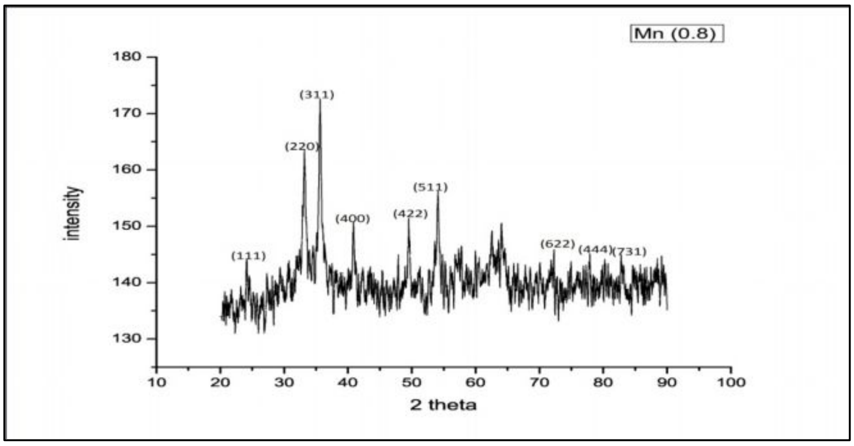


Figure 1(c):Graph obtained from XRD studies on $Mn_{0.8}Fe_{0.2}Fe_2O_4$ nanopowder

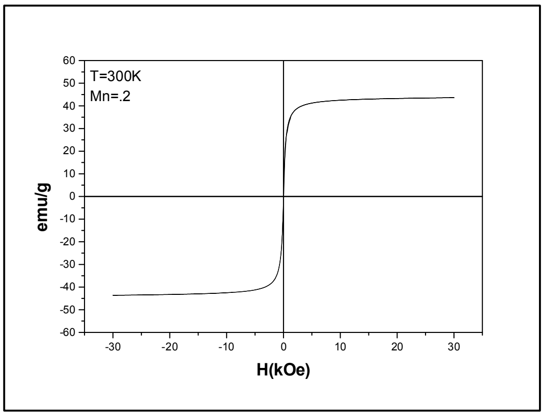
VSM studies:

Magnetic Hysteresis loop traced by VSM, showed zero looploss, Near zero coercivity, Near zero remanence hysteresis. These properties are hinting towards super paramagnetic behavior.The reason for obtaining superparamagnetic particles can be explained by the anisotropy temperature equivalence

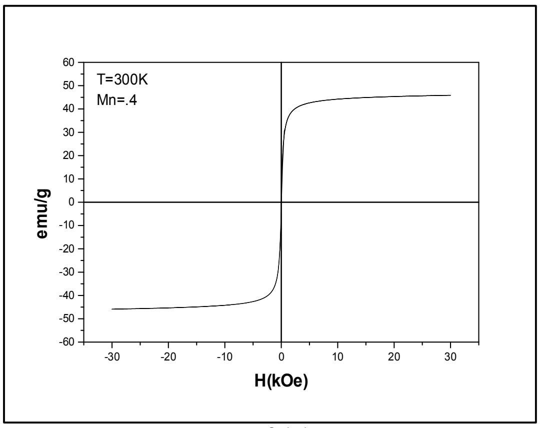
$$K_uV = K_BT \qquad (3)$$

where K_u is anisotropy constant and K_B is Boltzmann constant

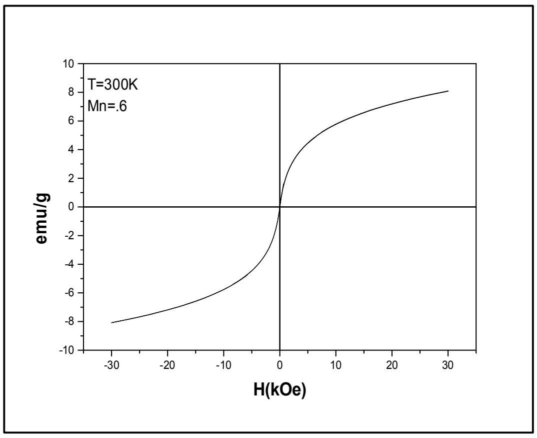
When the volume of the nanoparticles is reduced beyond a limit, magnetic anisotropy also changes. Hence the LHS of the equation will approach zero. Hence, at room temperature itself, complete randomization of spins will occur and hence these particles are formed as super paramagnetic[6, 9, 10].



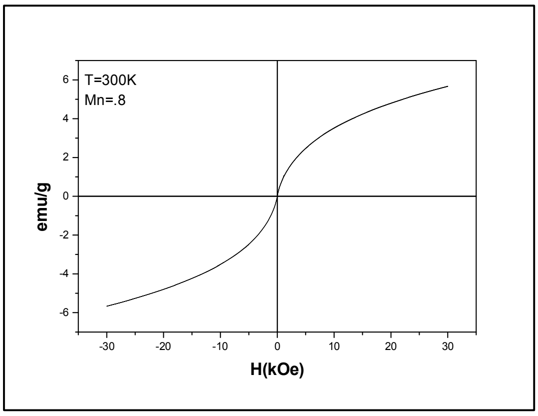
2(a)



2(b)



2(c)



2(d)

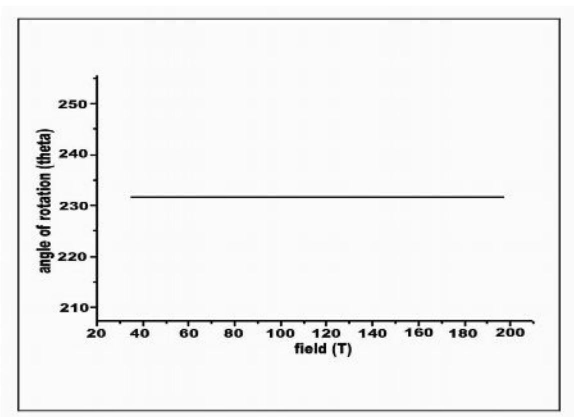
Figure: Graph obtained from VSM studies showing the superparamagnetic nature of the 2(a)$Mn_{0.2}Fe_{0.8}Fe_2O_4$, 2(b) $Mn_{0.4}Fe_{0.6}Fe_2O_4$, 2(c)$Mn_{0.6}Fe_{0.4}Fe_2O_4$, 2(d)$Mn_{0.8}Fe_{0.2}Fe_2O_4$

Magneto optical studies:

As the field increases the angle of rotation is found to increase up to a certain limit after that it appears to be a constant. This can be explained as follows. At low to moderate concentrations of ferrofluids, when a magnetic field is applied parallel to the ferrofluid film, particles will form aggregates which grow in the direction of magnetic field in the form of thin pillar like columns as the magnetic field of lines are from one pole piece to the second one. The chain formation dynamics depends mainly on the magnetic field values and the sweep rates. The samples with higher concentrations get saturated in higher applied fields. Hence the magneto optical signals also get saturated in higher applied fields[7].

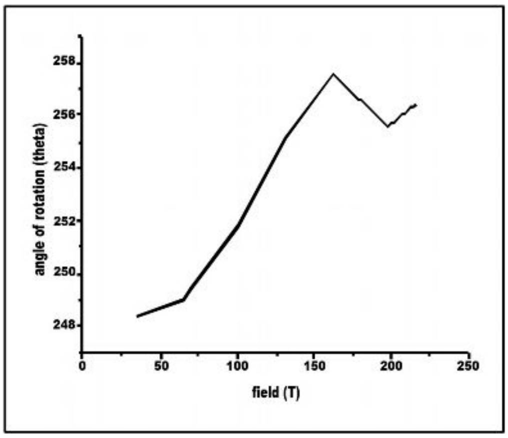
Reference Reading Terpentine alone

Field	Angle of rotation
35	231.5
66	231.5
99	231.5
132	231.5
163	231.5
197	231.5
217	231.5



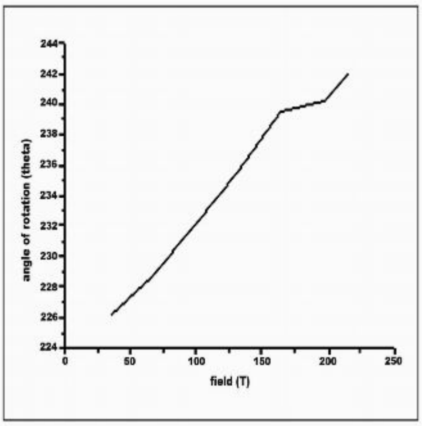
1. Optical Properties of manganese ferrite ferrofluid (*$Mn_{0.2}Fe_{0.8}Fe_2O_4$*)

Field	Angle of rotation
35	248.4
66	249
99	251.6
132	255.2
163	257.5
197	255.6
217	256.5



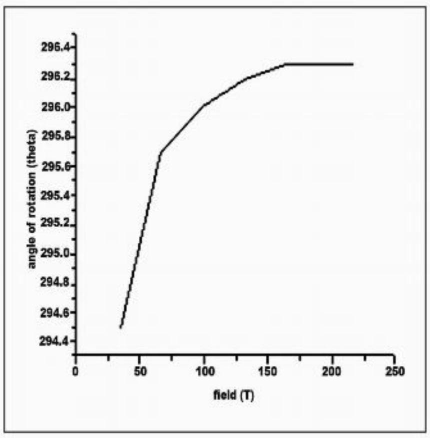
2. Optical properties of manganese ferrite ferrofluid *($Mn_{0.4}Fe_{0.6}Fe_2O_4$)*

Field	Angle of rotation
35	226.2
66	228.6
99	232
132	235.6
163	239.5
197	240.2



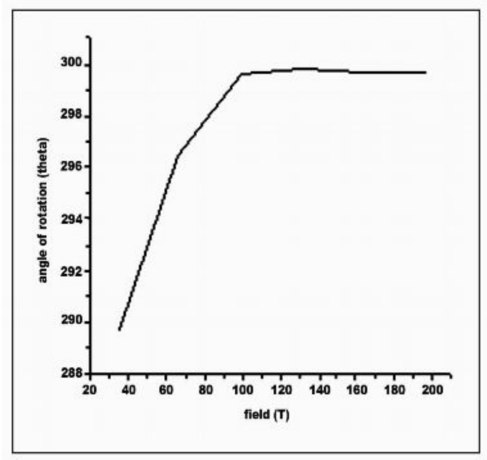
3.Optical properties of manganese ferrite ferrofluid (*$Mn_{0.6}Fe_{0.4}Fe_2O_4$*)

Field	Angle of Rotation
35	**294.5**
66	**295.7**
99	**296.26**
132	**296.3**
163	**296.3**
197	**296.3**
217	**296.3**



4. Optical properties of manganese ferrite ferrofluid ($Mn_{0.8}Fe_{0.2}Fe_2O_4$)

Field	Angle of rotation
35	289.7
66	296.4
99	299.6
132	299.8
163	299.7
197	299.7
217	299.7



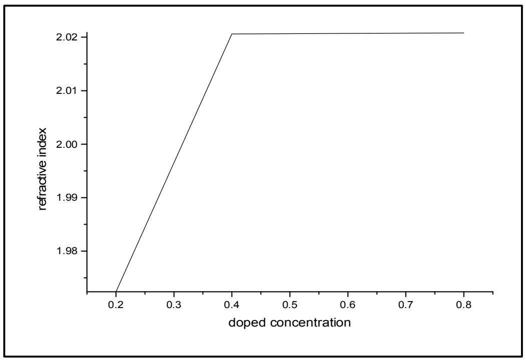
Refractive index vs. composition:

Refractive index of the ferrofluid depends on the doping concentration. As more and more Mn ions are substituted for the Fe ions, refractive index shows an increasing trend and finally it approaches a saturation value. It is calculated by using deviation method[7]. This is due to the modified optical band structure upon the foreign metal substitution in the magnetite lattice.

Refractive indices manganese ferrite ferrofluid($Mn_xFe_{1-x}Fe_2O_4$)

Absence of magnetic field

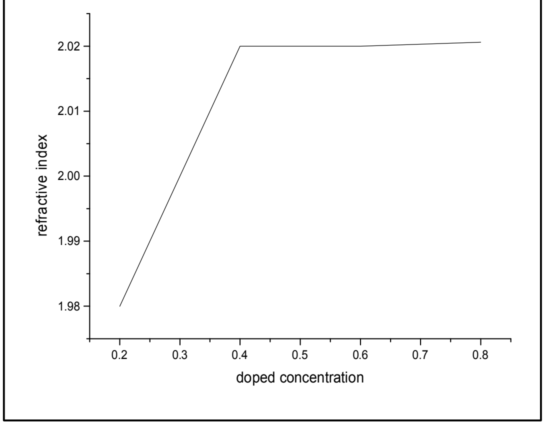
Doped concentration	Refractive indices
0.2	1.9724
0.4	2.0206
0.6	2.0207
0.8	2.0208



Refractive indices manganese ferrite ferrofluid($Mn_xFe_{1-x}Fe_2O_4$)

Presence of magnetic field

Doped concentration	Refractive indices
0.2	1.98
0.4	2.020
0.6	2.02
0.8	2.020684753



Refractive indices manganese ferrite ferrofluid($Mn_xFe_{1-x}Fe_2O_4$)

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Conclusion

Ferrofluids are one of the important classes of nanomaterials because of their controllability in flow and physical properties with the application of magnetic field. In the current investigation, manganese substituted ferrite ferrofluids prepared by co-precipitation are analyzed by different techniques. The structural characterization using XRD showed that the samples are polycrystalline with almost negligible impurities. Magnetization studies showed that they are superparamagnetic with negligible loop loss owing to the smaller dimensions of the suspended particles. The magnetic field dependence of refractive index and optical properties like specific rotation confirmed the controllability of physical properties of these fluids with applied magnetic field.

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