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Synthesis and Characterization of Manganese Substituted Aqueous Ferrofluid

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Abstract: Manganese substituted manganese ferrofluids of different concentrations have been prepared by co-precipitation method. Characterizations of samples were done by X-Ray diffraction (XRD), Vibrating Sample Magnetometer (VSM), UV-VIS spectrophotometry and photoluminescence spectroscopy. Tetramethylammonium hydroxide (TMOAH) was used as surfactant and water as the carrier fluid. X-Ray diffraction studies showed the polycrystalline structure of the sample. Crystalline size is found to be in the range of 6nm-12nm. Magnetic properties were analyzed using Vibrating Sample Magnetometer showed large saturation magnetization which increases with increase in concentration of manganese. This is due to cation distribution in ferrite where Mn^{2+} replaces the Fe^{3+} from tetrahedral sites to octahedral sites. This results a structural transition in superparamagnetic manganese ferrite from normal to inverse spinel structure.

Keywords: Synthesis and Characterization of Manganese Substituted Aqueous Ferrofluid.

Introduction

Ferrofluids are the interesting magnetic liquids that can be controlled by an external magnetic field. They are the colloidal suspensions of single domain (region in which electrons spins are similarly oriented) magnetic particles with dimensions of about ten nanometer dispersed in a liquid carrier.

NASA was the first to develop and characterize ferrofluids[1] in 1960's.Since then there have been several applications[2] for ferrofluids in industrial as well as technological fields such as magnetic memory, inkjet printers magnetic seals etc. They are well known for their biomedical applications like MRI contrasting agents, hyperthermia, targeted drug delivery in tumor cells and cancer cells, anti bacterial activity etc.

Manganese ferrofluid posses cubic spinel structure and has been extensively used in various applications. Composition, morphology and size of the magnetic particles determine the property of ferrofluid. Manganese ferrite has soft magnetic properties[3] such as low coercivity and moderate saturation magnetization. It has mechanical hardness and good chemical stability also. Properties of manganese ferrofluid arise from the redistribution of cations (bivalent and trivalent) in tetrahedral and octahedral sites.

Synthesis of manganese ferrite nanoparticles by solvothermal method was explained by Li-Xia Yang et al. In this the structural characterizations[4] were done by using X-ray diffraction. S.K.Vyawahare et al[5] reported structural and magnetic properties of spinel system contain manganese using X-ray diffraction and magnetization. F.W.Harrison et al[6] discussed about the cationic distribution and magnetic moments of the manganese ferrite nanoparticles.

In this paper, $MnFe_2O_4$ is synthesized by co-precipitation method by using water as the carrier fluid and Tetramethylammonium hydroxide (TMAOH) as surfactant[7].

Experimental Details

Synthesis of Manganese Substituted Aqueous Ferrofluid

Samples of Manganese ferrofluid ($Mn_x\ Fe_{1-x}\ Fe_2O_4$) for x=0.2, 0.4, 0.6 were synthesized by co-precipitation method. $FeCl_2$ (1.988g, 1M) and $FeCl_3$ (3.244g, 2M) and $MnCl_2$ (0.3958g, 0.2M) each of 10ml were mixed together. NH_4OH is added drop by drop to the mixture until the formation of black precipitate. Surfactant, Tetramethylammonium hydroxide (TMAOH) is added for the stabilization. The formed precipitate was dried in order to get the manganese ferrite nanoparticles and was dispersed in carrier fluid, water. For the synthesis of different concentrations of manganese ferrite, $MnCl_2$ was taken as 0.7916g and 1.1874g for 0.4M, 0.6M respectively, and the same procedure is repeated. All the preparations were done at room temperature.

Structural studies

Structural studies[8] have been undergone using Rigaku D maxC X-ray diffractometer with Cu-Kα line ($\lambda = 1.5406A^0$). Lattice planes were identified by comparing experimental pattern to that of JCPDS data ((JCPDS PDF # 10-0319). Crystalline size is also estimated.

Magnetic Studies

Magnetic studies of powered samples were done by quantum design Vibrating Sample Magnetometer (VSM). It gives the change of magnetization (M_s) with the magnetic field strength (H). Hysteresis loop is studied and saturation magnetization (M_s) is measured from the M-H curve obtained.

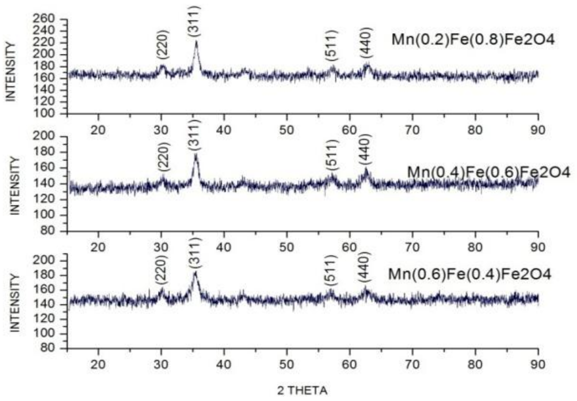
Results and Discussion

Structural studies:

Manganese substituted magnetite of three different concentrations were synthesized by co-precipitation method. The grain size is measured from Full Width at Half Maximum (FWHM) of diffraction peak by using Debye-Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where D is the crystalline size, λ is the wavelength of radiation, θ is the angular width (in radians) which is equal to FWHM. The XRD peaks can be tabulated into the spinel cubic lattice type. It represents polycrystalline structure of the manganese substituted ferrofluid.XRD shows broadening of the diffraction peaks due to lower grain size. Crystalline size is found to be in the range 6nm to 12nm.



VSM Studies:

Magnetic properties of different concentrations of the powdered sample were measured using Vibrating Sample Magnetometer (VSM). The obtained M-H curves show near zero coercivity and near zero remanence which indicates the super paramagnetic property of the samples.

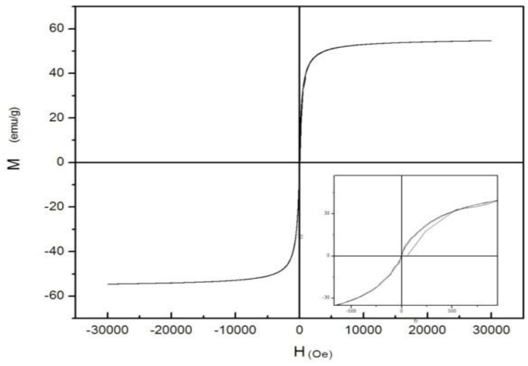


Fig.4.M-H curve for (Fe $_{(0.8)}$ Mn $_{(0.2)}$ Fe$_2$O$_4$)

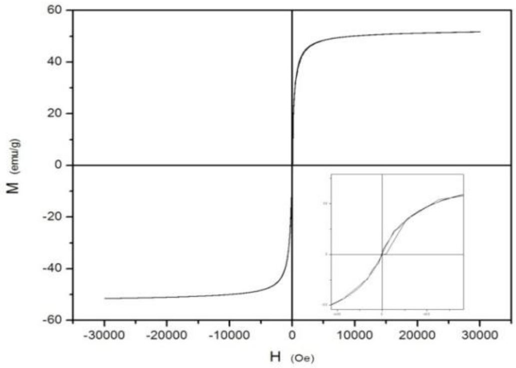


Fig.5.M-H curve of (Fe $_{(0.6)}$ Mn $_{(0.4)}$ Fe$_2$O$_4$)

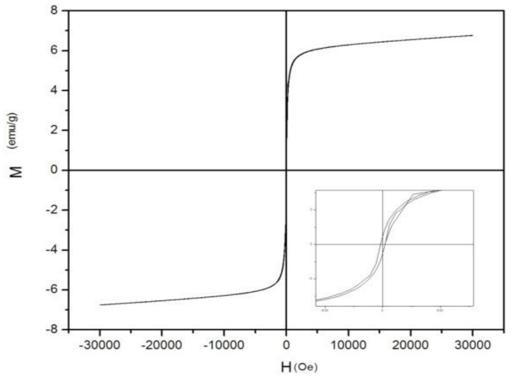


Fig.6.M-H curve of (Fe $_{(0.4)}$ Mn $_{(0.6)}$ Fe_2O4)

The Saturation magnetizations of the sample (Fe $_{(0.8)}$ Mn $_{(0.2)}$ Fe_2O_4) is 43.754 emu/g, for (Fe $_{(0.6)}$ Mn $_{(0.4)}$ Fe_2O_4) 46.302 emu/g and for (Fe $_{(0.4)}$ Mn $_{(0.6)}$ Fe_2O_4) it is 48.015 which is greater than the other two samples.

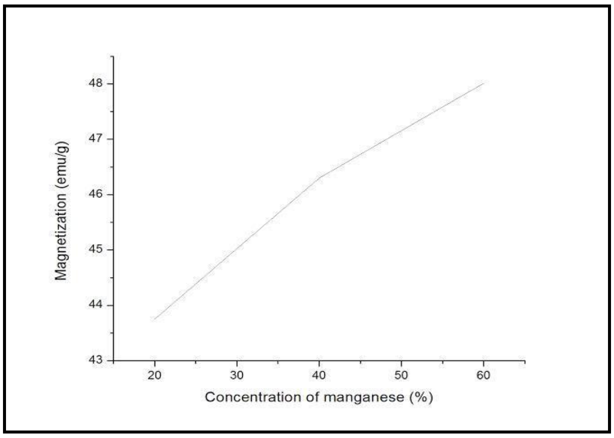


Fig.7 Variation of Saturation Magnetization with concentration of Manganese

This above results shows that saturation magnetization increases with increase in concentration of manganese. The experimental magnetic moments of the samples were obtained by the equation[5, 9],

$$^{n}{}_{B} = \frac{\sigma s * molecular\ weight}{5585}$$

Where σ_s is the saturation magnetization.

The magnetic moments the samples were obtained as 1.806$\mu_{B,}$ 1.912 μ_B, 1.92 μ_B (for Mn = 0.2.0.4, 0.6 respectively) indicates that the value of magnetic moment gradually increases with increase in concentration of manganese. This is explained by using the cation redistribution in manganese ferrite.

When concentration of Mn increases, Mn^{2+} replaces Fe^{2+} from tetrahedral site (A site) which increases the magnetization of the sample (for the Manganese ferrite observed magnetic moment is 4.6μ_B-5μ_B, where as for ferrous ion 4μ_B and for Mn^{2+} it is 5μ_B[3]. Further substitution of manganese leads to the replacement of Fe^{3+} (5 μ_B) from octahedral (B) site to tetrahedral (A) site. This condition enhances inverse spinel structure in which Mn^{2+} occupies 1/4 of octahedral and Fe^{3+} occupies 1/8 of tetrahedral and 1/4 of octahedral sites with moments are arranged in anti-parallel direction indicates the super paramagnetic behavior. In spinel lattice system the interaction[10, 11] between A and B sub lattices consists of inter-sub lattice (A-B) super exchange interaction, intra-sub-lattice (A-A) interaction and exchange interaction (B-B). Studies shows inter-sub-lattice super exchange interactions(A-B) of the cations are much stronger than (A-A)and (B-B) sub-lattice interactions .When the accumulation of Fe^{3+} are increased in A site the interaction between Fe_A^{3+}-Fe_B^{3+} increases which is nearly twice stronger compared to Mn_A^{2+} - Fe_B^{3+} interaction. This can results in the increase of saturation magnetization of manganese ferrite. The observed values of saturation magnetization of the samples are expressively lower than that of the reported value of $MnFe_2O_4$ (80emu/g). The decrease in saturation magnetization of the samples compared to that of bulk is due to the surface effects in these samples.

Conclusion

Manganese substituted aqueous ferrofluids were synthesized with Tetramethylammonium hydroxide (TMAOH) as stabilizer and water as carrier fluid. The average grain size of the ferrofluids was in the range 6-12nm. Pure manganese ferrite is a normal spinel (80%) while magnetite is an inverse spinel. Hence the system with increasing manganese content can give normal to inverse spinel structure transition with super paramagnetic behavior.

References

1. Patricia Berger, Katie J. Beckman, Dean J. Campbell, Arthur B. Ellis, Madison, George C. Lisensky, Preparation and properties of aqueous ferrofluid, Journal of Chemical education, 1999, 76,943-948.
2. D Carta, P Floris, A Falqui, G Mountjoy, A Boni, C Sangregorio, A Corrias, Synthesis and micro structure of manganese ferrite colloidal nanocrystals, Phys.Chem.Chem, Phys, 2010, 12, 5074-5083.
3. Alex Goldman, Modern Ferrite Technology, Springer, USA, 51-61.
4. Li-Xia Yang, Feng Wang, Yan-Feng Meng, Qing-Hua Tang, and Zi-Qi Liu, Fabrication and Characterization of Manganese Ferrite Nanospheres as a Magnetic Adsorbent of Chromium, Journal of Nanomaterials, 2013, 293464, 1-5.
5. S K Vyawahare, N R Shamkuwar& Madan C Sable, Structural and magnetic properties of $Mn_{1+x}Si_xFe_{1-x}Cr_{1-x}O_4$ system, Indian Journal of Pure and Applied Physics, 2005, 43, 545-56.
6. F. W. Harrison, W. P. Osmond, and R. W. Teale , Cation Distribution and Magnetic Moment of Manganese Ferrite ,Phys.Rev,1957,106,865.
7. J. Popplewell, Technological Applications of Ferrofluids, Phys. Technol, 1984, 15,150-156.
8. Daliya S. Mathew, Ruey-Shin Juang ,An overview of the structure and magnetism of spinel ferrite nanoparticles and their synthesis in micro emulsions, Chemical Engineering, 2007,129,51-56.
9. O. M. Hemeda, Structural and Magnetic Properties of $Co_{0.6}ZnN_{0.4}Mn_xFe_{2-x}O_4$, Turk J Phys, 2004, 28, 121 – 132.
10. C.Scherrer, A.M Figueiredo Neto, Ferrofluids: Properties and applications, Brazilian Journal of Physics, 2005, 35,718.
11. M. Goodarz Naseri, E. Bin Saion, H. Abbastabar Ahangar, M. Hashim, A.H. Shaari Synthesis and characterization of manganese ferrite nanoparticles by thermal treatment method, Journal of Magnetism and Magnetic Materials, 2011, 323, 1745–1749.

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