EXPERIMENTAL INVESTIGATIONS ON NANO FERROFLUIDS

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The present work on the title *"Experimental Investigations on Nano Ferrofluids"* is on the basis of an investigation carried out by the author in the Department of Physics, Thiagarajar College, Madurai, India, during the period 2012-2019 towards the doctoral degree in Physics. The thesis is broadly divided into seven chapters. The salient features of each chapter are given below. The author has published some of these investigations in various international journals and conferences (Appendix I).

CHAPTER – I

Introduction

In this chapter, a brief account on classification of magnetic materials and especially ferrimagnetic material is given as these are useful in high density magnetic recording, tunable optical filters, ferrofluids, etc., [1]. Iron oxide nanoparticle is one of the most useful ferrimagnetic material as it possesses superparamagnetism with high values of magnetization and hence a brief review about ferrites is provided. In addition, nano ferrofluids also find applications such as hyperthermia, coolant in loud speakers, magnetic seals, optical filters, etc., [2]. Hence an introduction about nano ferrofluid is also given.

Now-a-days magnetic nanoparticles are used in high frequency applications as they experience low losses [3]. Hence, the nature of non-interacting single domain nanoparticles with the process of magnetization are discussed. Cubic spinel structure and superparamagnetic property of magnetic nanoparticles are also presented. Magneto viscous effect of ferrofluids without and with applied magnetic fields are discussed. The two basic relaxation mechanisms of the magnetic nanoparticles suspended in ferrofluids namely Brownian and Neel's relaxation process are also discussed for the better understanding of ferrofluids [4].

Motivation and the reason for choosing the effect of pH and dopants like cobalt, magnesium, zinc, manganese for investigations are discussed in this chapter.

CHAPTER – II

Synthesize and characterization of ferrofluids of different pH values

In this chapter, the effect of pH values on the properties of magnetic iron oxide nanoparticles are investigated. In the co-precipitation method of preparing nanoparticles pH values are playing a major role in determining the crystallite size and its related properties. So, the effect of pH values on the properties of iron oxide nanoparticle are studied. Various studies on the properties of iron oxide nanoparticles are reported in literature [5], where changes in crystalline parameters and properties are observed. C.R. Lin et al., [6] investigated the magnetic properties of iron oxide nanoparticles synthesized by thermal decomposition method. It was reported that saturation magnetization and coercive field of the nanoparticles are observed to be dependent on their particle size. Further, they reported that the temperature dependent magnetic measurement showed that iron oxide nanoparticle exhibits superparamagnetic behavior at room temperature. Rohollah Safi et al., [7] investigated the effect of pH on the particle size and magnetic properties of cobalt ferrite nanoparticle synthesized by co-precipitation method. It was observed that crystallite size and degree of crystallinity increases with the pH values. Magnetic properties of the nanoparticle were reported to be more for nanoparticles with larger crystallite size. S. Brojabasi et al., [8] investigated the effect of hydrodynamic particle size on the light transmission characteristics of ferrofluids containing surface treated Fe_3O_4 nanoparticles. They used poly-acrylic acid, tetra-methyl ammonium hydroxide and phosphates for surface treatment of the nanoparticles. Surfactant adsorbed varies the hydrodynamic particle size, which influences the particle chain formation and zippering effect. As a result, their magneto-optical property can be tuned.

In the present work, initial structural investigation using X-ray diffraction technique are discussed. Structural changes occurring due to variation of pH values are discussed with crystallite size and lattice constant. Surface morphology investigations of the Fe_3O_4 magnetic nanoparticles using Scanning electron microscope and Transmission electron microscope are discussed. Chemical composition of the samples obtained using energy dispersive analysis of X-rays are presented to confirm the cations present in the samples. Magnetic parameters of the nanoparticles are dependent on their crystallite size, hence an increase in crystallite size increases the magnetic properties. Samples synthesized at higher pH values exhibit more magnetic properties. Magnetic properties of the samples like saturation magnetization, remanence and coercivity using vibrating sample magnetometer are discussed. The variation of Faraday rotation of Fe_3O_4 nanoferrofluids with applied magnetic flux density are discussed. Faraday rotation is found to be more for samples synthesized at higher pH values.

CHAPTER – III

Synthesize and characterization of cobalt doped iron oxide ferrofluids

In the chapter, the effect of doping cobalt ion with iron oxide nanoparticles are investigated. Addition of cobalt ion increase the magneto crystalline anisotropy and magnetic parameters of the nanoparticles. Various studies on the properties of cobalt doped iron oxide nanoparticles are reported in literature [9]. Sichu Li et al., [10] carried out a study on the effect of Co^{2+}/Fe^{2+} ratio on the structural and magnetic properties of the nanoparticles. It was also reported that coercivity and blocking temperature of the nanoparticles vary with Co^{2+}/Fe^{2+} ratio. Mohamed et al., [11] reported that the sintering temperature increases the crystallite size of cobalt ferrite nanoparticles synthesized by organic acid precursor method. Increase in crystallite size increases the saturation magnetization of the nanoparticles. Synthesize and properties of cobalt ferrite nanoparticles was studied by B.G. Toksha et al., [12]. It was reported that the particle size of the nanoparticle increases with annealing temperature. Further, the existence of anisotropy of the nanoparticles might be attributed to surface effects, which leads to increased coercivity. It was also reported that the saturation magnetization of cobalt ferrite nanoparticle increases with increase in particle size.

In the present work, $Co_xFe_{3-x}O_4$ nanoparticles were synthesized using co-precipitation method and their initial characterizations were done using XRD, SEM, TEM and EDAX. Substitution of cobalt cations alters the structural properties and magnetic properties of the samples. Crystallite size increases with cobalt ion substitution because of its preferential site occupancy. Replacement of iron ion by cobalt ion with different atomic radii changes the lattice parameter. Magneto crystalline anisotropic nature of cobalt ions are responsible for bringing out changes in the magnetic properties. Room temperature magnetic properties measured using VSM are discussed in this chapter. Saturation magnetization value decreases with cobalt substitution because of the changes in exchange interaction existing between tetrahedral site and octahedral site. Coercivity of the nanoparticle increases because of the substitution of anisotropic cobalt cations. Variation of Faraday rotation as a function of applied magnetic flux density are discussed.

CHAPTER – IV

Synthesize and characterization of cobalt doped magnesium ferrofluids

In this chapter, cobalt ion is used as dopant in magnesium ferrite, to tune their properties. Cobalt cation have preferential octahedral site occupancy and pronounced magnetocrystalline anisotropy. As a result of cobalt addition, structural, magnetic and magneto-optical properties are expected to be changed. Various studies related to the properties of cobalt substituted magnesium ferrite nanoparticles are reported in the literature [13]. Franco et al., [14] studied the effect of magnesium ions substitution on the magnetic properties of cobalt ferrite nanoparticles synthesized by forced hydrolysis method and reported that room temperature magnetic measurement indicates that these nanoparticles are superparamagnetic. It was reported that the blocking temperature of the magnesium doped cobalt ferrite nanoparticles decreases. Also, it was reported that the effective magnetic anisotropy decreases with the addition of magnesium ions. Chandra et al., [15] carried out magnetic and mossbauer studies on cobalt substituted magnesium ferrite prepared by sol-gel method and reported that the hysteresis loop measurement indicates that the nanoparticles are superparamagnetic at room temperature. Also, it was reported that increasing magnesium cations decreases the saturation magnetization and coercive field, because of the decrease in anisotropy energy of the nanoparticles. Further they reported that remanent magnetization of magnesium doped cobalt ferrite decreases because of lesser exchange interactions and Mossbauer measurement indicates that the nanoparticles are ferrimagnetic.

In the present work, characterizations such as XRD, SEM, TEM, EDAX, magnetic measurements and magneto-optical properties are done. The decrease in crystallite size and increasing lattice constant of the nanoparticles are discussed with cobalt concentration. Replacement of non-magnetic magnesium ions by cobalt ions are responsible for bringing changes in their magnetic properties. Magnetic parameters of the sample varying with the cobalt substitution are measured using vibrating sample magnetometer and discussed. Magneto-crystalline anisotropic nature of cobalt ion was used to tune the magnetic properties of $Co_xMg_{1-x}Fe_2O_4$ nanoparticles. Increasing the content of cobalt ion increases the coercive field of the nanoparticles. Faraday rotation of $Co_xMg_{1-x}Fe_2O_4$ nanoferrofluid increases with cobalt substitution and are discussed in this chapter.

CHAPTER – V

Synthesize and characterization of zinc doped cobalt ferrofluids

Cobalt ferrite nanoparticles with high magnetization and moderate coercivity are used for high density magnetic recording. In this chapter, we studied the effect of adding zinc cations in cobalt ferrite to modify its properties. Zinc ion is chosen because of its property to occupy tetrahedral site replacing iron ions. This nature of cations may possibly be used to tailor their properties. Also, we studied the magneto-optical properties which vary with zinc substitution. Various studies related to the properties of zinc substituted cobalt ferrite nanoparticles are reported in the literature [16]. Duong et al., [17] synthesized zinc substituted cobalt ferrite nanoparticles by forced hydrolysis method, which exhibits superparamagnetic behavior at room temperature and have ferrimagnetic behavior below blocking temperature. They reported that saturation magnetization, remanence and coercivity of the nanoparticle decreases with addition of zinc content, which may be attributed to the enhanced spin canting effect at the surface in zinc rich samples. M.U. Islam et al., [18] carried out a study on the properties of zinc substituted cobalt ferrite nanoparticles prepared by ceramic technique. It was reported that addition of non-magnetic zinc decreases the saturation magnetization and remanence values of the nanoparticles, which may be attributed to the weakening of exchange interaction existing between tetrahedral and octahedral sites. With the addition of zinc, frustration and randomness of the spin increases and the value of coercivity increases.

In the present work, XRD technique is used to confirm the crystal structure formed. The decrease of crystallite size with substitution of zinc is discussed. The replacement of cobalt cation (atomic radii 0.078 nm) by zinc cation (atomic radii 0.082 nm) increases the lattice parameter, which is in agreement with Vegard's law. Surface morphology investigations of the nanoparticles using SEM and TEM are discussed in this chapter. The non-magnetic zinc cations preferentially occupying tetrahedral site modifies the magnetic properties such as saturation magnetization, remanence and coercive field of the nanoparticles. Magnetic properties of the nanoparticles measured with vibrating sample magnetometer are discussed. Magnetic properties are observed to decrease with the addition of zinc ions. Faraday rotation of the $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluid varies as a function of magnetization and the values measured for various magnetic flux densities are discussed.

CHAPTER – VI

Synthesize and characterization of zinc doped manganese ferrofluids

Now-a-days manganese ferrites are used in high frequency applications because of their low loss. Tuning the properties of manganese ferrite is one of the important factor to make it suitable for any particular applications. In this chapter, non-magnetic zinc is used as dopant to vary the magnetic properties of manganese ferrite. Addition of zinc varies the magnetic properties including their structural, electrical and magneto-optical properties. Various studies related to the properties of zinc substituted manganese ferrite nanoparticles were reported in the literature [19]. E. Veena Gopalan et al., [20] carried out investigations on the properties of manganese zinc ferrite nanoparticles prepared by chemical co-precipitation method and reported that addition of zinc content decreases the crystallite size and lattice parameter of the nanoparticles, which may be attributed to the cation distribution and atomic radii of cations respectively. Also, it was reported that magnetic properties of manganese zinc ferrite decreases with zinc content. M.R. Syue et al., [21] investigated the electrical and magnetic properties of manganese zinc ferrites synthesized by combustion method and reported that with the substitution of manganese cation, crystallite size decreases but lattice parameter increases. Also, it was reported that the room temperature magnetic properties of the nanoparticle exhibits superparamagnetism and the values are increasing with manganese substitution.

In the present work, structural characterization of the samples obtained using X-ray diffraction pattern are discussed. The decrease of crystallite size with zinc substitution is discussed. Replacement of manganese cation (atomic radii 0.091 nm) by zinc cation (atomic radii 0.082 nm) decreases the lattice parameter, which is in agreement with Vegard's law. Surface morphology investigations of the samples with the aid of electron microscopy are presented and discussed. Chemical composition of the nanoparticles obtained using EDAX are discussed in this chapter. Replacement of manganese ions by non-magnetic zinc cation modifies super-exchange interaction existing between the cations of two sub-lattices and as a result magnetic properties of the nanoparticle varies. Magnetic parameters of the samples measured at room temperature using VSM technique are discussed. Magnetic properties of the nanoparticles are found to decrease with zinc substitution. The decrease in measured Faraday rotation of $Mn_{1-x}Zn_xFe_2O_4$ ferrofluids with zinc substitution are discussed in this chapter.

CHAPTER – VII

Summary

The seventh chapter summarizes all the results obtained in our work. It includes the discussion of structural and magnetic properties of Fe_3O_4 nanoparticles synthesized at different pH values using co-precipitation method. Structural and magnetic properties of $Co_xFe_{3-x}O_4$ nanoparticles, $Co_xMg_{1-x}Fe_2O_4$ nanoparticles, $Co_{1-x}Zn_xFe_2O_4$ nanoparticles and $Mn_{1-x}Zn_xFe_2O_4$ nanoparticles are discussed. Faraday rotation of ferrofluids prepared using these nanoparticles are also discussed.

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Appendix – I

List of publications

[1] Study of Faraday effect on $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick**, K. Ramachandran and R Srinivasan, Nanosystems: Physics, Chemistry, Mathematics, 7 (2016) 624-628.

[2] Study of magneto-optic effect on $Mn_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick**, K. Ramachandran and R Srinivasan, AIP Conference Proceedings 1731 (2016) 130054.

[3] A study on impact of zinc substitution on magneto-optic properties of manganese ferrite nanoferrofluids, **R. Karthick** and R. Srinivasan, Journal of Magnetism and Magnetic Materials, 441 (2017) 443-447.

[4] A study on magneto-optic properties of $Co_xMg_{1-x}Fe_2O_4$ nanoferrofluids, **R. Karthick**, K. Ramachandran and R Srinivasan, AIP Conference Proceedings 1942 (2018) 130049.

[5] A study on effect of cobalt on Faraday rotation of $Co_xFe_{3-x}O_4$ nanoferrofluids, **R. Karthick** and R. Srinivasan communicated to Journal of Magnetism and Magnetic Materials.

[6] A study on Faraday rotation of cobalt substituted zinc ferrite nanoferrofluids, **R. Karthick** and R. Srinivasan communicated to Materials Chemistry and Physics.

Papers presented in conferences

[1] Magnetic and electrical characterization of $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluids synthesized by co-precipitation, **R. Karthick** and R. Srinivasan, International conference on Nanoscience and Engineering (ICONSEA – 2014), Jawaharlal Nehru University, Hyderabad, held during 26-28 June 2014.

[2] Synthesis and Characterization of $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick** and R. Srinivasan, International conference on Perspectives in vibrational spectroscopy (ICOPVS – 2014), Mar Ivanios College, Trivandrum, held during 8-12 July 2014.

[3] Magnetic and Electrical studies of $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick** and R. Srinivasan, National Seminar on Recent Trends in Crystal Growth and Nano Materials (NSCGNM-2014), National College, Trichy, held during 7-9 August 2014.

[4] Study of Faraday effect on $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick**, K. Ramachandran and R. Srinivasan, International Conference on nanomaterials and Nanotechnology (NANO-2015), KSR College, Thiruchengode, held during 7-10 December 2015.

[5] Study of Magneto-optic effect on $Mn_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick**, K. Ramachandran and R. Srinivasan, 60^{th} DAE-SSPS symposium, AMITY University, Noida, held during 21-25 December 2015.

[6] A study on the magneto-optic properties of $Ni_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick** and R. Srinivasan, International Seminar on Nanoscience and Technology (ISNST-2016), Mother Teresa Women's University, Kodaikanal, held on 20 September 2016.

[7] A study on the magneto-optical properties of $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluids, **R. Karthick** and R. Srinivasan, 1^{st} International Conference on Nanoscience and Nanotechnology, VIT University, Vellore, held during19-21 October, 2016.

[8] A study on the effect of pH values on magneto-optic properties of Fe_3O_4 nanoferrofluids, **R. Karthick**, K. Gangadevi and R. Srinivasan, International Conference on Functional Materials (ICFM), Thiagarajar College, Madurai, held during 7-8 September 2017.

[9] A study on the magneto-optic properties of $Co_{0.5}Zn_{0.5}Fe_2O_4$ and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ nanoferrofluids, **R. Karthick,** K. Gangadevi and R. Srinivasan, International conference on Advanced Functional Materials for Energy, Environment and Biomedical Applications (AFMEEB - 2017) at Madurai Kamaraj University, Madurai, held during 11-12 December 2017.

[10] A study on magneto-optic properties of $Co_xMg_{1-x}Fe_2O_4$ nanoferrofluids, **R. Karthick**, K. Ramachandran and R. Srinivasan, 62nd DAE-SSPS symposium, BARC, Mumbai, held during 26-30 December 2017.

[11] A study on the effect of pH values on magneto-optic properties of Fe_3O_4 nanoferrofluids, **R. Karthick**, P. Chitralekha, K. Gangadevi, K. Ramachandran and R. Srinivasan, MRSI National Symposium on "Advances in Functional and Exotic Materials" jointly organized by MRSI – Trichy Chapter and the Centre for High Pressure Research, Bharathidasan University, Tiruchirappalli, held during 14-16 February 2018.

[12] A study on the magneto-optic properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ and $Mg_{0.5}Zn_{0.5}Fe_2O_4$ nanoferrofluids, **R. Karthick**, K. Gangadevi and R. Srinivasan, National Conference on Recent Advanced Materials (NCRAM - 2018), Thiruvalluvar University College of Arts & Science (TVUCAS) Campus, Thennangur, held during 23-24 February 2018.

[13] A study on the impact of zinc substitution on the Faraday effect of nickel ferrite ferrofluids, **R. Karthick** and R. Srinivasan, International conference on Advanced Nanomaterials for Energy, Environment and Healthcare Applications (ANEH – 2018), K.S.R. College of Arts and Science for Women, Thiruchengode, held during 31st August and 1st September 2018.