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Study of Faraday effect on $Co_{1-x}Zn_xFe_2O_4$ nanoferrofluids

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Zinc doped cobalt ferrite$Co_{1-x}Zn_xFe_2O_4$ nanoparticles ($x = 0.1$, 0.5, 0.9) were synthesized by chemical co-precipitation method. The crystallite size, which was calculated from the full width half maximum (FWHM) value of the strongest peak (311) plane using Scherer approximation, was found to decrease with higher zinc content. The surface morphology of the powder samples was obtained using transmission electron microscopy (TEM). Magnetic properties, such as Saturation magnetization (M_s), Remanent Magnetization (M_r) and Coercivity of the powder samples, were measured using Vibrating Sample Magnetometer (VSM) at room temperature and were found to decrease with increased zinc content. Aqueous ferrofluids prepared from the powder samples were subjected to magnetic field to measure their Faraday rotation. Faraday rotation of the ferrofluids was found to increase with applied magnetic field and decrease with increasing zinc composition.

Keywords: nanoferrofluid, vibrating sample magnetometer, faraday rotation.

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1. Introduction

Ferrofluids are a colloidal suspension of single domain magnetic particles, with typical dimensions of about 10 nm, dispersed in a carrier liquid [1]. To avoid the aggregation of nanoparticles, they have to be covered with a suitable surfactant. Optical property of ferrofluids can be altered by external applied magnetic field [2]. Structural reorientation of the nanoparticles suspended in a magnetic colloid brings out magneto-optic properties [3], which are used in developing optical sensors [4], photonic devices [5], etc. The kinetics of particle aggregation in magnetic nanofluid have been studied using various techniques [6, 7]. The functional group adhered to the nanoparticles (stabilizers) can influence the kinetics of magnetic field induced chain like formation which influences their magneto-optic properties [8]. Among other influencing parameters, the dipolar interaction among nanoparticles is the main driving force for particle aggregation and field induced structural transitions [9]. Common methods of synthesis of ferrofluids employ co-precipitation [10], ball milling [11], sol-gel method [12] and micro emulsion [13]. Among these methods, co-precipitation is the low cost and less energy required for synthesis of ferrofluids.

2. Sample preparation

The chemical co-precipitation method was used to synthesize $Co_{1-x}Zn_xFe_2O_4$ nanoparticles for $x = 0.1$, 0.5 and 0.9. Stoichiometric ratios of $FeCl_{3.6}H_2O$, $CoCl_2$ and $ZnCl_2$ solution were mixed and added to NaOH solution under constant stirring. Diluted HCl was added until the pH reaches 9. In order to prevent agglomeration of the nanoparticles, oleic acid was added. The resultant precipitates were isolated by centrifugation and washed with de-ionized water, acetone and ethanol to remove impurities and then dried at 60 °C for 4 hours. Powder samples were used to carry out initial characterization such as XRD, TEM and VSM. Then, aqueous nanoferrofluids were prepared to study their magneto-optic effect.

3. Results and discussion

3.1. X-ray diffraction

The XRD pattern of the powder samples are shown in Fig. 1, which confirm the spinel structure (JCPDS no 22-1086) [14]. The crystallite size for each composition was calculated using the Debye-Scherer formula for the (311) plane. The crystallite size decreases from 11.4 nm to 5.6 nm with an increase in zinc content. In spinel ferrite, zinc ions have stronger preference to occupy tetrahedral site, iron ions preferentially occupy tetrahedral site while cobalt ions have octahedral site preference [15]. Increasing x values in $Co_{1-x}Zn_xFe_2O_4$ spinel ferrite causes zinc ions to occupy tetrahedral sites preferentially, displacing iron ions from the octahedral sites [16]. Therefore, replacement of cobalt ions by zinc ions forces the transformation of inverse spinel into normal spinel structure.

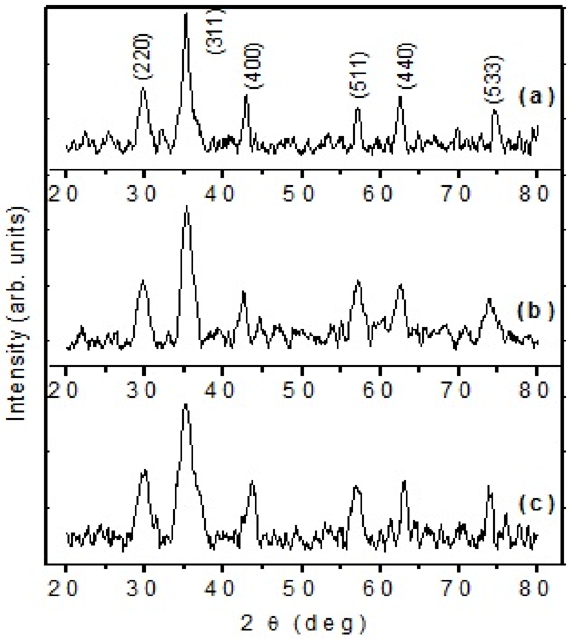

FIG. 1. XRD pattern of the samples (a) $Co_{0.9}Zn_{0.1}Fe_2O_4$, (b) $Co_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $Co_{0.1}Zn_{0.9}Fe_2O_4$

3.2. Transmission electron microscopy

Figure 2 shows the transmission electron microscope (TEM) images of $Co_{1-x}Zn_xFe_2O_4$ nanoparticles. Physical particle sizes of the samples are found to be slightly larger than the crystallite size obtained by XRD. It was also observed that the presence of surfactant and decrease in the magnetic moment of particles reduced magnetic nanoparticle aggregation.

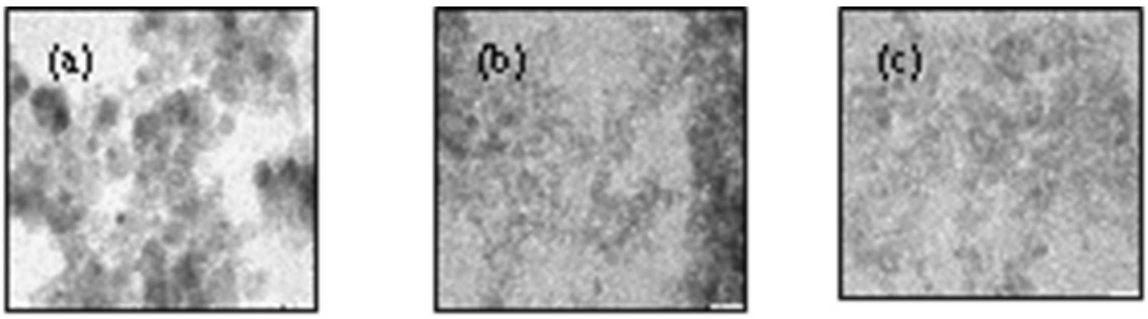

FIG. 2. TEM of the samples (a) $Co_{0.9}Zn_{0.1}Fe_2O_4$, (b) $Co_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $Co_{0.1}Zn_{0.9}Fe_2O_4$

3.3. Magnetic measurements

M-H loop of the powder samples are shown in Fig. 3. Magnetization in a spinel ferrite arises as a result of dominant interaction existing between tetrahedral (A) site and octahedral (B) site mediated by oxygen A-O-B interactions [17]. Increasing zinc content in $Co_{1-x}Zn_xFe_2O_4$ spinel ferrite causes zinc ions to occupy tetrahedral sites and displaces iron ions to octahedral sites [16]. In octahedral sites, cobalt ions are replaced by iron ions [18]. Thus, the substitution of non-magnetic zinc ion varies the A-O-B interaction. Magnetic parameters, such as saturation magnetization (M_s), remanent magnetization (M_r) and coercive field (H_c), were found to vary with zinc content and are shown in Table 1. The values are in agreement with the literature [19]. Moreover, saturation magnetization of bulk cobalt ferrite is 65 emu/g [20]. Coercivity is a measure of magnetocrystalline anisotropy of

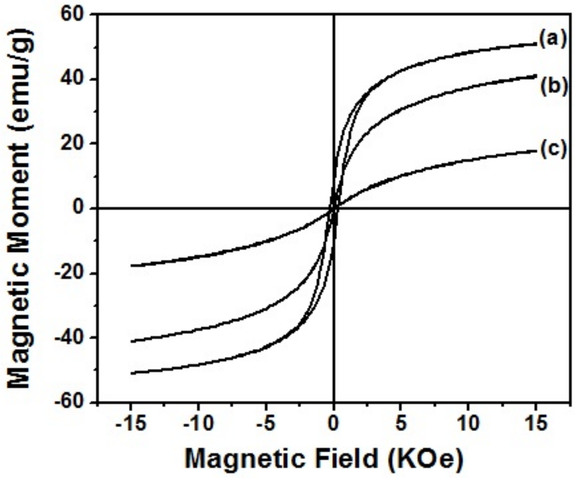

FIG. 3. M-H loop at room temperatureof the samples (a) $Co_{0.9}Zn_{0.1}Fe_2O_4$, (b) $Co_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $Co_{0.1}Zn_{0.9}Fe_2O_4$

the samples [17]. Decreasing values of coercivity and remanence at room temperature indicate that the samples are approaching superparamagnetism [21]. Surface defects, such as formation of dead layer, canting of particle surface spins and deviation in cation distribution may reduce the magnetic properties [15].

TABLE 1. Magnetic parameter of the samples

Samples	Saturation Magnetization (emu/g)	Remanent Magnetization (emu/g)	Coercive Field (KOe)
$Co_{0.9}Zn_{0.1}Fe_2O_4$	50.95	9.4350	0.2878
$Co_{0.5}Zn_{0.5}Fe_2O_4$	41.04	0.0638	0.0044
$Co_{0.1}Zn_{0.9}Fe_2O_4$	17.89	0.0046	0.0013

3.4. FaradayrRotation

Faraday rotation of the samples was measured using standard technique, which includes electromagnet, polarizer, analyzer, cuvette and a monochromatic sodium vapor lamp. $Co_{1-x}Zn_xFe_2O_4$ nanoparticles were dispersed in de-ionized water and sonicated for 30 minutes. The volume fraction was kept as 0.005 for all the samples. Linearly polarized light from a polarizer was allowed to pass through the electromagnet, ferrofluid and an analyzer. In this set-up, a magnetic field applied is longitudinal to the polarized light. Light emerging out from analyzer was detected using a photodetector. The angle of rotation (θ_F) of plane polarized light is proportional to the product of applied magnetic field (B) and optical path length (l) of the ferrofluid through which the light passes:

$$\theta_F = VBl,$$

where, V is Verdet constant of the sample.

When a magnetic field is applied to the samples, degeneracy is lifted and the relative energies are determined by Lande g factor. During the transition of electrons between degenerate states, rotation of plane of polarization is accompanied by the development of an ellipticity of the originally polarized light [22]. Also, it was reported that Faraday rotation can be enhanced due to crystal field transitions and intervalence charge transfer transitions between neighboring ions [22, 23]. Varying the occupancy of tetrahedral and octahedral sites changes the Faraday rotation. The variation of Faraday rotation and Verdet constant are shown in Fig. 4 and Fig. 5. Variation of Verdet constant below 600 gauss for samples (a) and (b) indicates the need to increase the accuracy of measurement system at low fields.

4. Conclusion

$Co_{1-x}Zn_xFe_2O_4$ nanoparticles were synthesized by co-precipitation method using oleic acid as surfactant. The XRD diffraction patterns confirm the cubic spinel structure. The crystallite size decreases with increased zinc

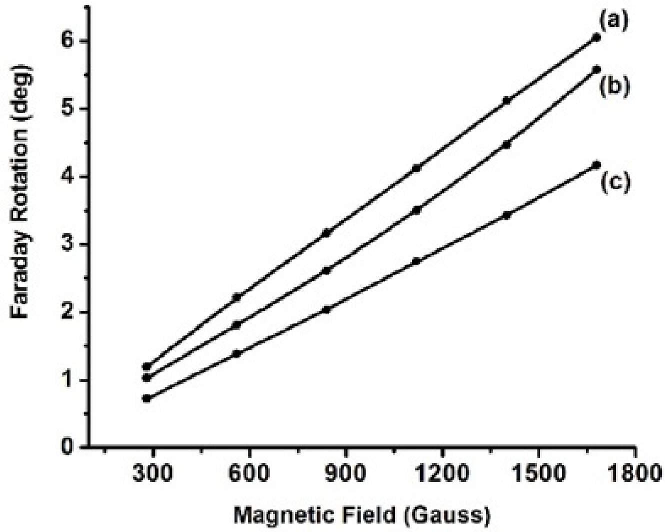

FIG. 4. Faraday rotation of the samples (a) $Co_{0.9}Zn_{0.1}Fe_2O_4$, (b) $Co_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $Co_{0.1}Zn_{0.9}Fe_2O_4$

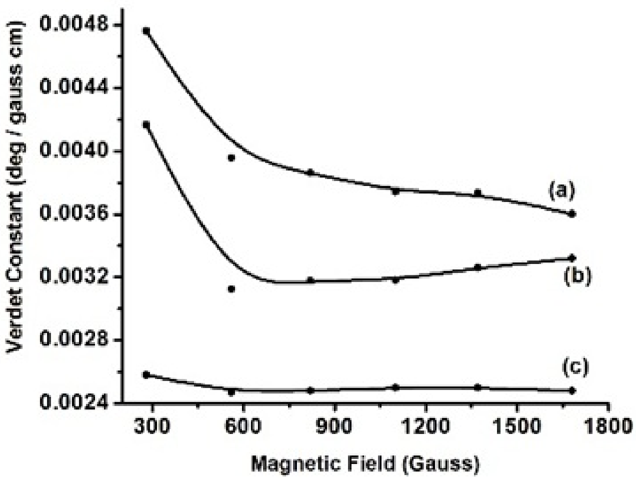

FIG. 5. Verdet constant vs magnetic field of the samples (a) $Co_{0.9}Zn_{0.1}Fe_2O_4$, (b) $Co_{0.5}Zn_{0.5}Fe_2O_4$ and (c) $Co_{0.1}Zn_{0.9}Fe_2O_4$

content. The magnetic properties and Verdet constant of $Co_{1-x}Zn_xFe_2O_4$ nanoparticles vary with the incorporation of zinc and cobalt ions into iron oxide spinel ferrite. The Faraday rotation and hence the Verdet constant decreases with increased zinc substitution.

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