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Structure of Co–Zn ferrite ferrofluid: A small angle neutron scattering analysis

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Abstract. A hydrothermal synthesis route is used to synthesize nanomagnetic particles of $Co_{0.3}Zn_{0.7}Fe_2O_4$ ferrite ferrofluids with particle diameter ranging from 5.5–9 nm. XRD analysis shows the formation of a single phase spinel structure. EDX results confirm the stoichiometric composition of the cations. Small angle neutron scattering technique is used to determine the size and size distribution of $Co_{0.3}Zn_{0.7}Fe_2O_4$ ferrofluid. The sizes thus obtained are in the range of 5.4 to 8.4 nm. These results are in agreement with magnetic measurements.

Keywords. Ferrofluid; nanocrystalline materials, small angle neutron scattering.

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1. Introduction

Different scattering techniques like dynamic light scattering, small angle X-ray scattering and small angle neutron scattering (SANS) are used to get information on the magnetic nanoparticles. All these techniques together give complementary information on the nanomaterials [1]. SANS with possibility to vary the contrast, is an ideal technique to determine the size of the magnetic particle, due to the high contrast between the magnetic particle core and the medium. In this paper we have used SANS technique to determine the size and size distribution of Co–Zn ferrofluid – a stable colloidal dispersion of nanomagnetic particles in a magnetically passive liquid – and compared with other techniques like, magnetometry, X-ray diffraction etc. Here we have synthesized $Co_{0.3}Zn_{0.7}Fe_2O_4$ magnetic nanoparticles of different sizes by varying pH and digestion time during synthesis. Particle size obtained using all these techniques are in agreement with each other.

2. Experimental

Nanomagnetic particles of $Co_{0.3}Zn_{0.7}Fe_2O_4$ were synthesized using hydrothermal synthesis technique. Aqueous solutions of salts of Co^{2+}, Zn^{2+} and Fe^{3+} were mixed

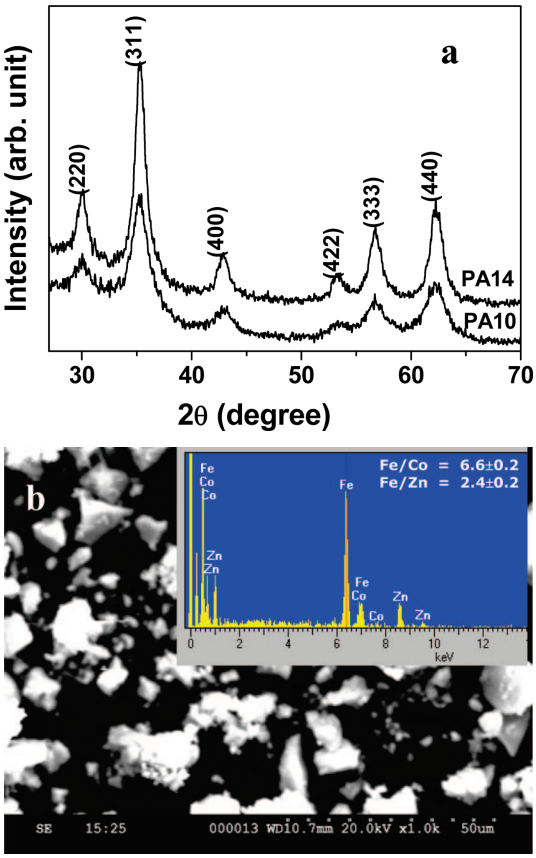

Figure 1. (**a**) XRD pattern of PA10 and PA14 and (**b**) SEM pattern of PA13 nanoparticles samples. Inset shows EDX pattern.

in stoichiometric proportion and with vigorous stirring this salt solution was added into 8 M NaOH solution at room temperature (see table 1). Precipitated particles were transferred to autoclave (NOVA Autoclave sterilizer, model no. 8533) and reaction was kept at inner pressure of 15±0.5 psi and temperature at 105±5°C. In this study four different sizes of Co–Zn ferrite particles were obtained by controlling the preparative parameters pH and digestion time (t_d). Digested particles were then removed from the autoclave and washed with distilled water to remove the salt impurities. These particles were coated with oleic acid and then dispersed in kerosene. The formation of single phase spinel structure was confirmed by D8 advanced model powder X-ray diffractometer (Bruker). The morphology and chemical compositions of the particles were analysed using Hitachi S-3000N scanning electron microscopy (SEM) and OXFORD D7021 energy dispersive X-ray (EDX) spectrometer. Magnetic measurements of magnetic fluids were carried out using a home-built magnetometer.

Table 1. Parameters derived from the XRD, magnetization and SANS studies.

	Preparation condition		X-ray parameters		Magnetization results @300 K			SANS results	
Samples	pH	t_{d} (min)	$D_{\mathrm{x}} \pm 0.1$ (nm)	$a \pm 0.001$ (nm)	D_{m} (nm)	σ_{m}	M_{d} (kA/m)	D_{s} (nm)	σ_{s}
PA10	10.5	30	5.5	0.8475	5.4	0.52	25	5.4	0.50
PA11	10.5	60	5.9	0.8438	5.8	0.44	28	6.1	0.55
PA13	11.6	30	6.8	0.8418	6.7	0.46	35	6.2	0.47
PA14	11.6	60	9.0	0.8431	8.9	0.43	45	8.4	0.60

D = Particle diameter. Suffixes x, m and s stand for XRD, magnetic and SANS results. σ is the deviation in $\ln(D)$ and M_{d} is the domain magnetization of particle. a = Lattice parameter, t_{d} = digestion time (min).

Small angle neutron scattering (SANS) measurements of Co–Zn magnetic fluids were carried out using SANS diffractometer at Dhruva reactor, Trombay, Mumbai, India [2]. The mean wavelength λ of the incident neutron beam is 0.52 nm with a wavelength resolution of ∼15%. The angular distribution of the scattered neutrons was detected (0.5–15^0) using a one-dimensional He^3 linear position sensitive detector (PSD). The accessible wave vector transfer $Q(= (4\pi/\lambda)\sin\theta/2$, where θ is the scattering angle) range of instrument is 0.18–3.0 nm^{-1}. The measured data have been corrected for room background and empty cassette contribution and normalized to a cross-section unit, using standard procedure.

3. Structure and morphology of nanomagnetic particles

Figure 1a shows typical XRD pattern of PA10 and PA14 samples. The pattern shows formation of single phase spinel structure. The intensity of all the peaks increases with increasing pH and digestion time reveals better crystallinity of the sample. Particle size calculated using Scherrer's formula for most intense (3 1 1) peak is given in table 1. It was observed that at low pH change in size of the particle with digestion time is less (∼10%) while it is high (>30%) at high pH. This indicates that at high pH the Ostwald ripening process is more active due to metal hydroxide dissolution.

Figure 1b shows polydispersed nature of PA13 nanomagnetic particles. The chemical composition was determined using EDX. The result confirms the stoichiometry of composition, i.e. Fe/Co = 6.6±0.2 and Fe/Zn = 2.4±0.2. Similar results were also obtained for other samples.

4. Results and discussion

4.1 *Magnetic measurements*

Figure 2 shows room temperature magnetization curve for PA13 and PA14 Co–Zn magnetic fluids. System exhibits zero coercivity and zero remanence at room temperature. The observed non-saturation behaviour is due to the size effect, i.e. applied field is not enough to saturate the system. In order to obtain the size and size distribution, the magnetization curve was fitted with modified Langevin's theory incorporating log-normal particle size distribution function [3] (solid line through the data points). The parameters derived from the fit are given in table 1. The particle size derived from the magnetization measurement agrees with that obtained from X-ray diffraction. $1/D$ dependence behaviour is observed in magnetization value (inset of figure 2).

4.2 *SANS measurements*

Small angle neutron scattering (SANS) experiment measures the coherent differential scattering cross-section $d\Sigma/d\Omega$ as a function of Q (momentum transfer vector).

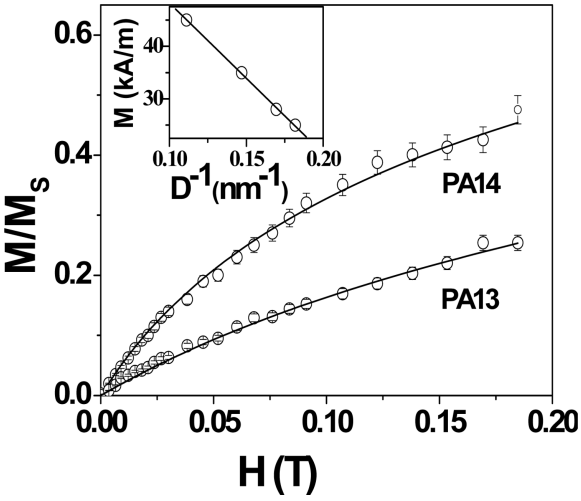

Figure 2. $M(H)$ curve for PA13 and PA14 samples.

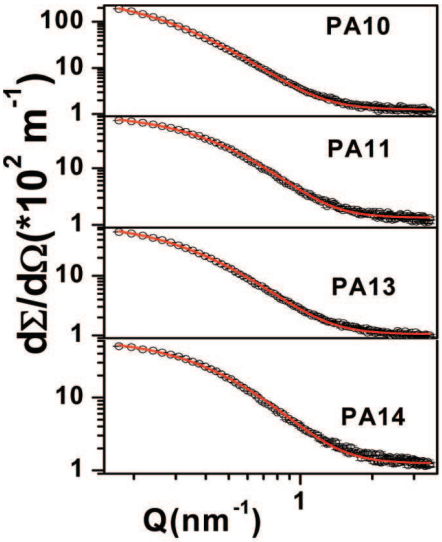

Figure 3. SANS pattern of Co–Zn magnetic fluids.

In the case of polydispersed system having log-normal size distribution, coherent differential scattering cross-section can be written as [4,5]

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q) = N(\rho_{\mathrm{P}} - \rho_{\mathrm{S}})^2 \int_0^\infty V^2 P(Q,D) S(Q) P(D) \mathrm{d}D, \tag{1}$$

where N is the number density of particles, ρ_{P} and ρ_{S} are the scattering length densities of particle and solvent respectively, $V(=\pi D^3/6)$ is the particle volume, $P(Q,D)$ is the particle form factor which depends on the shape and size of the

particle, $S(Q)$ is the interparticle structure factor, which depends on the spatial arrangement of particles and is thereby sensitive to interparticle interactions and $P(D)\mathrm{d}D$ is the log-normal particle size distribution function. For a dilute system $S(Q)$ is unity and hence interparticle interference effects are negligible giving only $P(Q, D)$ dependency in SANS pattern. The scattering length density of the surfactant, oleic acid (0.0776×10^{14} m^{-2}) was found to be very small compared to that of the particle (5.98×10^{14} m^{-2}) and carrier (kerosene) (0.189×10^{14} m^{-2}), hence was neglected in the computation. In the present case, the magnetic scattering length density is one order of magnitude lesser than the nuclear scattering length density of the particles. In addition, the magnetic property of the sample is very weak at room temperature. Hence, only nuclear scattering length density is considered for the calculation. SANS data of Co–Zn magnetic fluid samples are shown in figure 3 where the line shows fit to eq. (1). The data are analysed assuming spherical particles. SANS results of magnetic fluid samples are given in table 1. The particle size obtained from SANS measurement is in agreement with those obtained from X-ray diffraction and magnetization measurements. One of the reason for the observed higher value of size distribution in SANS compared to magnetization measurement is the limited coverage in scattering angles or in neutron momentum transfer in SANS experiment. This gives a truncation error in measured correlation function and hence distribution differs.

5. Conclusion

Nanomagnetic particles and magnetic fluids of Co–Zn ferrite have been synthesized using hydrothermal synthesis technique. These nanoparticles and magnetic fluids have been characterized using XRD, SEM, EDX, magnetization and SANS. Particle sizes determined using three different techniques, i.e. X-ray diffraction, magnetization and SANS are in agreement with each other.

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