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Magnetic field-induced cluster formation and variation of magneto-optical signals in zinc-substituted ferrofluids

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Abstract

Fine magnetic particles (size≅100 Å) belonging to the series $Zn_xFe_{1-x}Fe_2O_4$ were synthesized by cold co-precipitation methods and their structural properties were evaluated using X-ray diffraction. Magnetization studies have been carried out using vibrating sample magnetometry (VSM) showing near-zero loss loop characteristics. Ferrofluids were then prepared employing these fine magnetic powders using oleic acid as surfactant and kerosene as carrier liquid by modifying the usually reported synthesis technique in order to induce anisotropy and enhance the magneto-optical signals. Liquid thin films of these fluids were prepared and field-induced laser transmission through these films was studied. The transmitted light intensity decreases at the centre with applied magnetic field in a linear fashion when subjected to low magnetic fields and saturate at higher fields. This is in accordance with the saturation in cluster formation. The pattern exhibited by these films in the presence of different magnetic fields was observed with the help of a CCD camera and was recorded photographically.

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1. Introduction

Ferrofluids are stable colloidal suspensions of ultrafine magnetic particles having a number density of $10^{23}/m^3$ in a base fluid [1]. Surfactant-separated ferrofluids have been extensively used for various applications due to their ease of preparation and greater stability against gravitational settling and agglomeration [2]. Here a steric repulsion is provided by the nonpolar tails of the surfactant uniformly coated on the fine magnetic particles having their particle size less than 100 Å. Such ultrafine particles exhibit Brownian motion if suspended in a carrier fluid [1,2]. They have potential industrial applications in making rotary seals, pressure sensors and loud speaker coolants [3].

Spinel ferrites attracted the attention of various researchers due to their excellent magnetic and electrical properties [4,5]. They are ideal materials for a variety of applications. Spinel ferrites can be in general depicted by the formula $(Me^{ii}_{\delta}\ Fe^{iii}_{1-\delta})[Me^{ii}_{1-\delta}\ Fe^{iii}_{1+\delta}]O_4$ where the cations inside the square brackets occupy octahedral sites (B) and those outside the brackets occupy the tetrahedral sites (A), when $\delta = 1$, the divalent cation occupy the A site and it is a normal spinel and when $\delta = 0$, it is an inverse spinel. At the nanolevel, these ferrites exhibit interesting phenomenon like single domain characteristics and super paramagnetism [6,7].

Ferrofluids exhibit many magneto-optical properties like field-induced optical birefringence, linear and circular dichroism, faraday rotation and ellipticity [8–17]. These

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measurements will help in throwing light on the phenomenon of formation of clusters in presence of an applied magnetic field. Controlled chain formation of assembly of magnetic particles dispersed in an appropriate carrier can yield magnetic gratings. Hence studies pertaining to magneto-optical properties of these fluids are important from a fundamental point of view.

A survey of literature reveals an absence of a systematic study on the optical properties of ferrofluidic thin films prepared from a series similar to $Zn_xFe_{1-x}Fe_2O_4$. In the literature most of the studies pertaining to the magneto-optical properties are based on magnetite-based ferrofluids. Magneto-optical studies on ferrofluids based on a ferrite belonging to the series similar to $Zn_xFe_{1-x}Fe_2O_4$ are absent in the literature or seldom reported. Moreover, a correlation of the observed optical properties of these ferrofluidic thin films with the magnetic properties of the precursors will throw a deeper insight on cluster formation under the influence of an external magnetic field.

In the present investigation, precursor magnetic samples belonging to the series $Zn_xFe_{1-x}Fe_2O_4$, where 'x' varies from 0.0 to 0.6 in steps of 0.1, are synthesized by cold co-precipitation technique. The technique of co-precipitation is modified to coat the surfactant and high-energy ball milling (HEBM) was employed for this.

The technique of HEBM was utilized so that the possibility of the modification of surface anisotropy exists here and this will enhance the magneto-optical signals. Fine magnetic powders thus synthesized by co-precipitation method were then subjected to HEBM with oleic acid and finally with kerosene to prepare ferrofluids. The structural properties of these precursor materials are studied. Ferrofluid liquid thin films were then prepared and field-induced laser transmission through these ferrofluid liquid thin films is studied for different compositions. Attempts are made to correlate their magnetic and corresponding optical properties. These results are presented here.

2. Experimental

2.1. Preparation of magnetic fine particles

Fine particle precursors belonging to the series $Zn_xFe_{1-x}Fe_2O_4$ were synthesized by the cold co-precipitation of the aqueous solutions of $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$ and $FeCl_3$ were taken in the appropriate molar ratio [18–20].

2.2. X-ray diffraction studies

X-ray diffraction (XRD) of the samples were recorded in an X-ray diffractometer (Rigaku Dmax-C) using Cu-Kα radiation ($\lambda = 1.5406$ Å). Lattice parameter (a) was calculated assuming cubic symmetry [21,22]. The average particle size of these powder samples was estimated by employing Debye Scherrer's formula

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

where λ is the wavelength of X-ray in Å, β the FWHM of the XRD peak with highest intensity in radians (when scattering angle 2θ is plotted against intensity), and D the particle diameter in Å.

2.3. Magnetization studies

The magnetic characterization of the fine particles were carried out using vibrating sample magnetometry (VSM) (Model: EG&G PAR 4500). The hysteresis loop is plotted and saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) were measured at room temperature.

2.4. Suspension of particles

The as-prepared particles were then subjected to HEBM by employing FRITSCH PULVERISETTE 7 PLANETARY MICRO MILL. In this, 800 rpm can be achieved and hence the momentum imparted to the particles will be very high. This helps to obtain a good suspension.

2.5. Ferrofluid preparation

Ferrofluids were then prepared by milling the powder samples prepared by cold co-precipitation first with the surfactant oleic acid for few minutes in a HEBM unit. The addition of oleic acid is to provide the necessary steric repulsion preventing the agglomeration of fine particles and thereby increasing the stability of the fluid. Finally the magnetic powder samples were milled with a base fluid kerosene to enhance the suspension of the fine particles. Then the samples were centrifuged at a speed of 3000 rpm and sonicated [1].

2.6. Ferrofluid film preparation

Liquid thin films of ferrofluids were made by sandwiching and encapsulating around 2 mm^3 of ferrofluid between two optically smooth and ultrasonically cleaned glass slides. The thickness of the fluid films is of the order of ~4000 Å. Thickness of the fluid film can be accurately measured using a travelling microscope. Concentration and thickness of the fluid film is kept constant for all set of samples to eliminate their effects.

This film was then suspended between the poles of a water-cooled electromagnet which can go up to a maximum magnetic field of 1 T. The ferrofluid film sample was irradiated with a polarized He–Ne laser having a power of 5 mW, and wavelength of 632 nm. The fluid film was aligned in such a way that the applied magnetic field is perfectly parallel to it. The laser beam is transmitted normally through the film sample and the transmitted light from the ferrofluid film sample was focused on to a