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

Swapna. S. Nair[a,*], S. Rajesh[a,1], V.S. Abraham[b], M.R. Anantharaman[a,*], V.P.N. Nampoori[c]

[a]Department of Physics, Cochin University of Science and Technology, Cochin 682 022, India
[b]School of Engineering and Sciences, International University of Bremen, 28759, Germany
[c]International School of Photonics, Cochin University of Science and Technology, Cochin-22, India

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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.

PACS: 75.20.Ck; 75.50.Gg; 75.50.Mm; 75.75.+a; 78.20.Ls; 78.66.Vs

Keywords: Ferrofluids; HEBM; Zinc ferrite; Field-induced assembling; Magneto-optics

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

*Corresponding authors. Tel.: +91 484 257740439; fax: +91 484 2532495.
E-mail addresses: swapna@cusat.ac.in (S.S. Nair), mraiyer@yahoo.com (M.R. Anantharaman).
[1]Present address: Biophysics and Microscopy Group, Molecular Cytology, University of Amsterdam, P.O. Box 94062,1090 GB Amsterdam, The Netherlands.

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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

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

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

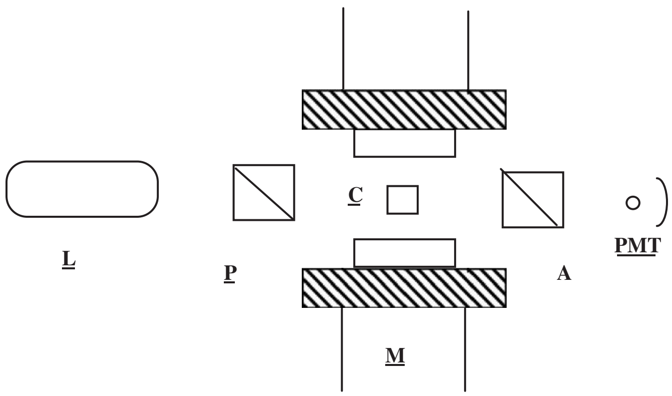

Fig. 1. Experimental set-up for field-induced laser transmission through the ferrofluid thin film. (normal incidence and detection with respect to the sample.)

white screen, placed at a distance of 0.25 m from the film. The experimental set-up is schematically shown in the Fig. 1. The sample concentration, field sweep rate and film thickness, and experimental set-up have been kept unaltered for all set of samples.

The intensity of the transmitted beam was measured using a laser power meter (OPHIR-PD 200) in the gradually increasing magnetic field. The exact field was measured each time with a digital Gaussmeter (Model DGM-102). The magnetic field was calibrated in terms of the optical output intensity for all these fluid film samples belonging to the series $Zn_xFe_{1-x}Fe_2O_4$.

2.7. Imaging of the chain formation

The thin ferrofluid film was kept in different magnetic fields and allowed to dry in the respective applied fields. These dried ferrofluidic thin films were viewed with the help of a CCD camera (Model no. G P KR 222) and an optical microscope and the pattern obtained was imaged on a colour video monitor and recorded photographically.

3. Results and discussion

A typical XRD spectrum is depicted in Fig. 2 ($Zn_{0.1}Fe_{0.9}Fe_2O_4$). The analysis of the XRD pattern indicates that the prepared compounds crystallize in the spinel phase. The particle size evaluation employing Debye Scherer's formula suggests that they lie in the range 50–95 Å for different samples with different zinc contents. The variation of particle size and lattice parameter is plotted with composition (x), which shows a linear behaviour in lattice parameter for the series $Zn_xFe_{1-x}Fe_2O_4$ (Figs. 3 and 4). This is in accordance with Vegard's law [4]. According to Vegard's law, the lattice parameter of a solid solution is directly proportional to the atomic percentage of the solute present in it. Here in the series $Zn_xFe_{1-x}Fe_2O_4$, as 'x' increases, the atomic percentage of 'Fe' decreases which reduces the lattice parameter value. The evaluation of the particle size is important at various

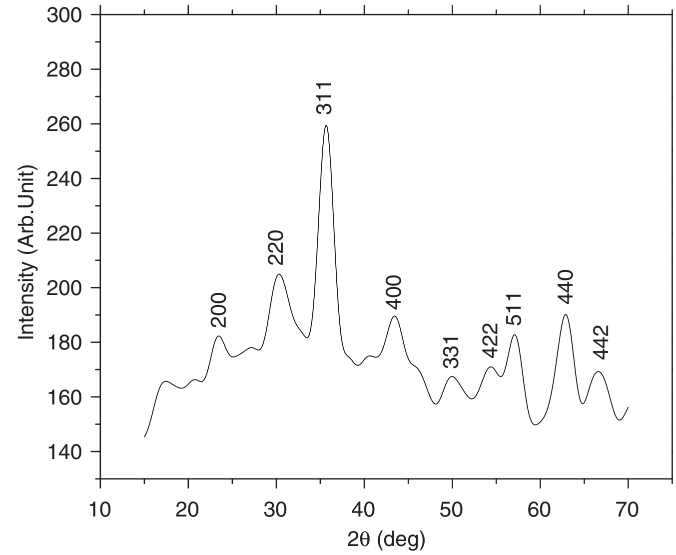

Fig. 2. X-ray diffraction spectrum of $Zn_{0.1}Fe_{0.9}Fe_2O_4$ ferrofluids.

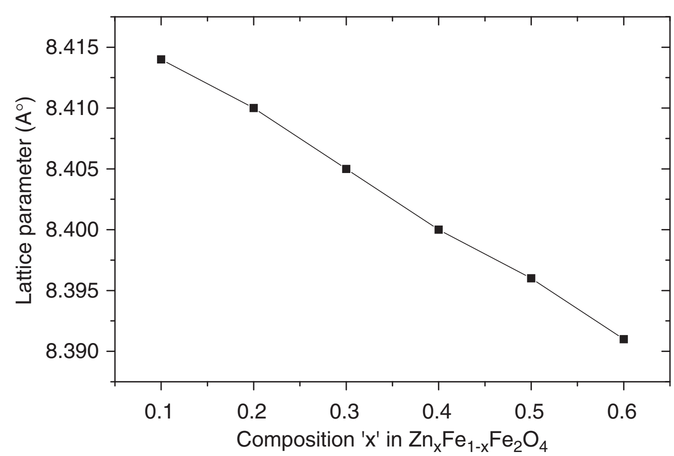

Fig. 3. Lattice parameter vs. composition.

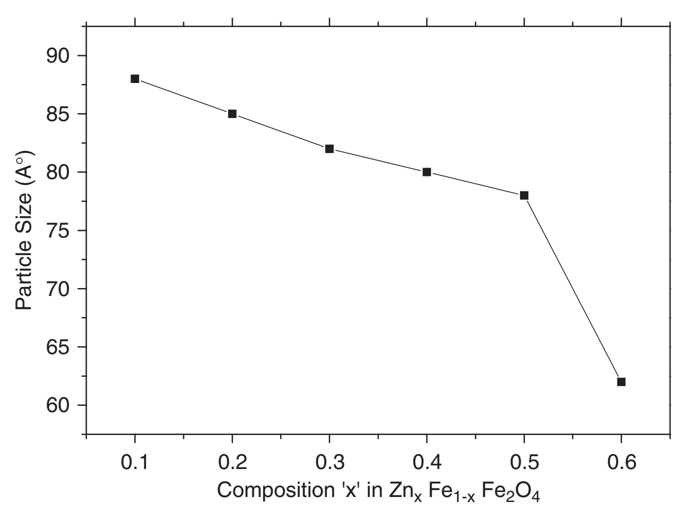

Fig. 4. Particle size vs. composition 'x'.

stages of milling in ferrofluid preparation as it controls many of the peculiar properties exhibited by these fluids and it has been shown that particles below a critical size of 100 Å will display single domain characteristics and super paramagnetism.

The magnetization of all the synthesized fine ferrite powder samples have been measured by VSM and the values fits well with the Neel's two sublattice model with an error percentage less than 2.5%. This small discrepancy may arise from the ultrafine characteristics of these ferrites. The samples have vanishing hysteresis with very low remanance which is a necessary criterion for a single domain/superparamagnetic particle. Neglecting interaction effects, the magnetization of these fine particles solely determine the magnetization of ferrofluids synthesized employing the same precursors and thus by knowing volume fraction of ferrites inside the ferrofluids, their magnetization can be calculated. Magnetization decreases as 'x' value increases in the series $Zn_xFe_{1-x}Fe_2O_4$ as predicted by the Neel's two sublattice theory. The magnetization curve for all the powder samples are shown in Fig. 5. The variation of measured as well as calculated saturation magnetization with 'x' value in the series $Zn_xFe_{1-x}Fe_2O_4$ is shown in Fig. 6.

The normalized output intensity versus applied magnetic field is plotted for the ferrofluid liquid thin films corresponding to $x = 0.1, 0.2, 0.3, 0.4, 0.6$. They are shown in Fig. 7. In very-low-field regime, in which the diffraction effects are negligible, almost linear variation of transmitted power is obtained when plotted against H^2 (Fig. 7 inset) and the nonlinearity begins to appear under small applied magnetic fields due to cluster formation and scattering (diffraction effects at very high applied fields) and they dominate thereafter. The square of saturation field H_s is determined for each of the composition (x) and are plotted for varying 'x'. They are depicted in Fig. 8.

As the ferrofluidic film restricts the motion of particles in a plane, application of a magnetic field increases structural

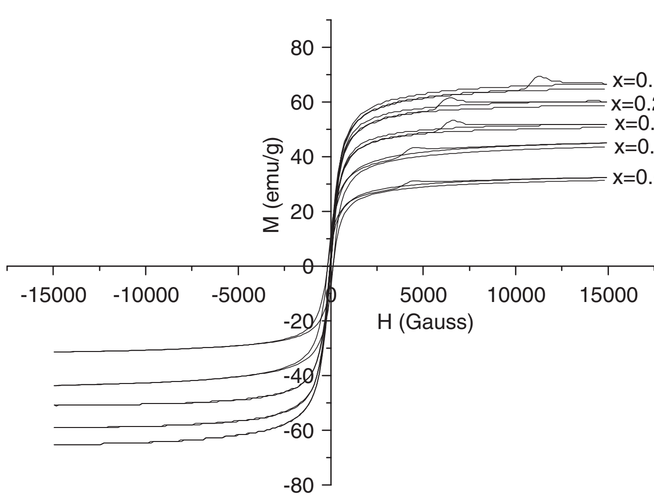

Fig. 5. Magnetization curves of the precursor samples belonging to the series $Zn_xFe_{1-x}Fe_2O_4$.

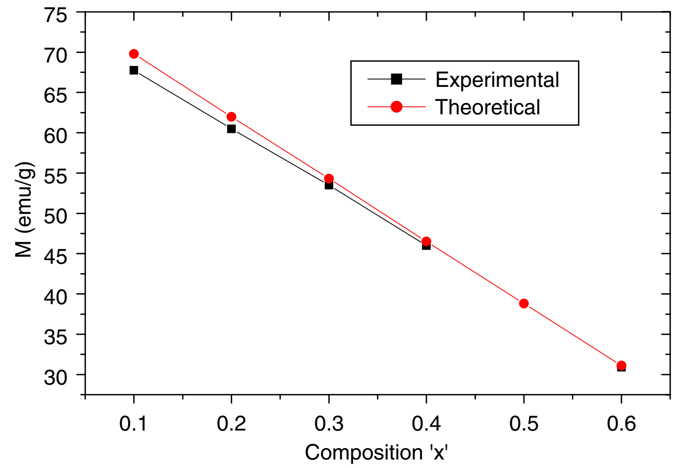

Fig. 6. Saturation magnetization vs. composition of the precursor powder samples belonging to the series $Zn_xFe_{1-x}Fe_2O_4$.

anisotropy of these particles and agglomeration starts at a very low magnetic field and the particles assemble themselves in the presence of the applied magnetic field, yielding long chains and this process gets saturated at higher fields giving rise to a two-dimensional quasi continuous thin wires [17,23–25]. This is an example of field induced assembling of nanomaterials.

The chain formation is confirmed by the photographs recorded at applied magnetic fields with the help of a CCD camera. Typical representative photographs are shown in Fig. 9a–d. Typical values of particle concentration in ferrofluids are 10^{13}–$10^{14}/mm^3$ with average particle size of about 100 Å in the absence of applied magnetic fields.

Using the CCD-imaged photographs, it is observed that under very small applied magnetic fields of the order of 100 G, no clusters have been observed with in the resolution of CCD camera. So the clusters formed are within the size limits of 1000 Å, and the clusters formed in these small applied magnetic fields consists of approximately 10 particles. So the size parameter

$$s = 2\pi rn/\lambda$$

is less than unity which is an essential criteria for Rayleigh scattering, where 'r' is the average radius of the scattering centre, 'n' is the refractive index of the carrier and 'λ' is the wavelength of light used in the low field limit.

At very low fields, clusters are so small in size and so 's' is much less than unity so that the extinction is dominated by absorption and the refractive index has its real part less than that of the imaginary part. So in the low-field regime, the scattering is Rayleigh scattering and the scattering intensity is very small to create any appreciable change in the transmitted intensity.

With moderate applied magnetic fields of the order of 250 G, the clusters become visible with in the resolution of CCD camera and the number of particles in those tiny clusters have been calculated assuming the average particle size. Number of particles along the breadth of the chain is of the order of 100 at 1400 G which becomes 600 at 4000 G

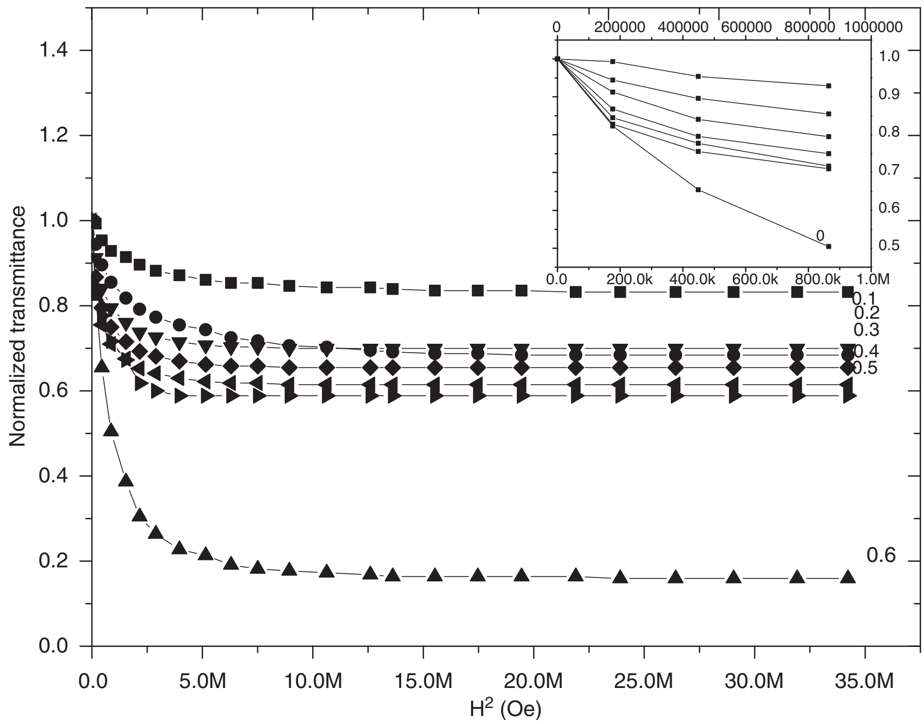

Fig. 7. Normalized power vs. square of the applied field (H^2) in ferrofluidic thin films based on $Zn_xFe_{1-x}Fe_2O_4$ (low-field values in the inset graph).

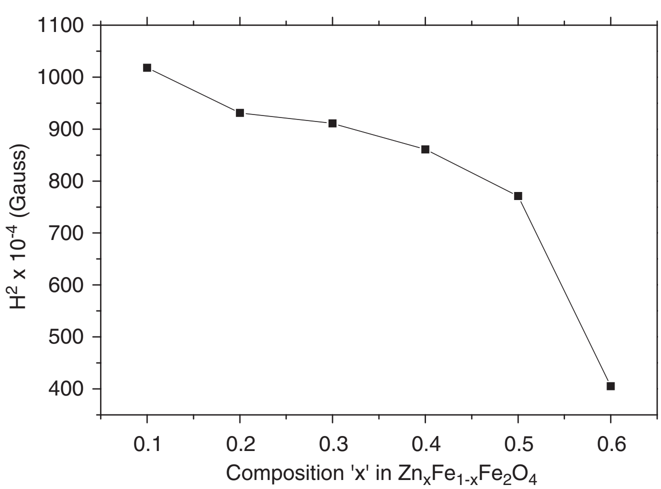

Fig. 8. Square of the saturation field (H^2) vs. composition 'x' in ferrofluidic thin films based on $Zn_xFe_{1-x}Fe_2O_4$.

which is the magnetic field for the saturated chain formation. Thus it can be concluded that the cluster formation saturates at higher fields giving rise to thin long chains of varying thickness leading to Mie scattering in the moderate magnetic fields and it changes to diffraction through narrow wires at saturating magnetic fields in which the chains formed are continuous. After this the transmitted intensity remains a constant.

The width of the chain further depends on the concentration of the samples. To eliminate the concentration dependence, all the fluids are kept at a constant concentration of 0.33. Furthermore the thickness of the film can also be a decisive factor.

Magneto-optical effects like birefringence and dichroism in any colloidal suspension may originate from the intrinsic optical anisotropy or the shape anisotropy of the fine magnetic particles suspended inside the ferrofluids. However, it is reported, from electron microscopic observations, that the shape anisotropy of the fine particles arising from the nonsphericity of particles is very small in ferrofluids in comparison with the large optical anisotropy created in the chain formation in the presence of applied magnetic field. No optical signal changes in zero applied fields for these surfactant-coated ferrofluids was observed [26–29]. In the magneto-transverse mode, the eigenmodes are linearly polarized waves making the dependence quadratic in applied magnetic field. This gives rise to linear birefringence dichroism, which contributes to the magnetic field-induced transmission in the magneto-transverse mode.

So as in the weak field approximation almost a linear variation for output intensity with H^2 is obtained for very low applied field. Here a deviation from the linear behaviour is observed at low applied field itself may be due to the preexisting clusters present in the fluid samples. Cluster formation dictates the scattered intensity from moderately high applied magnetic fields and the diffraction effects are dominated. The transmitted intensity remains steady after the saturation in cluster formation [29,30].

The particle size dependence of ferrofluids on these optical and magneto-optical properties is quite relevant from the fundamental point of view. A graph is plotted with the particle size and the 'x' values in the series

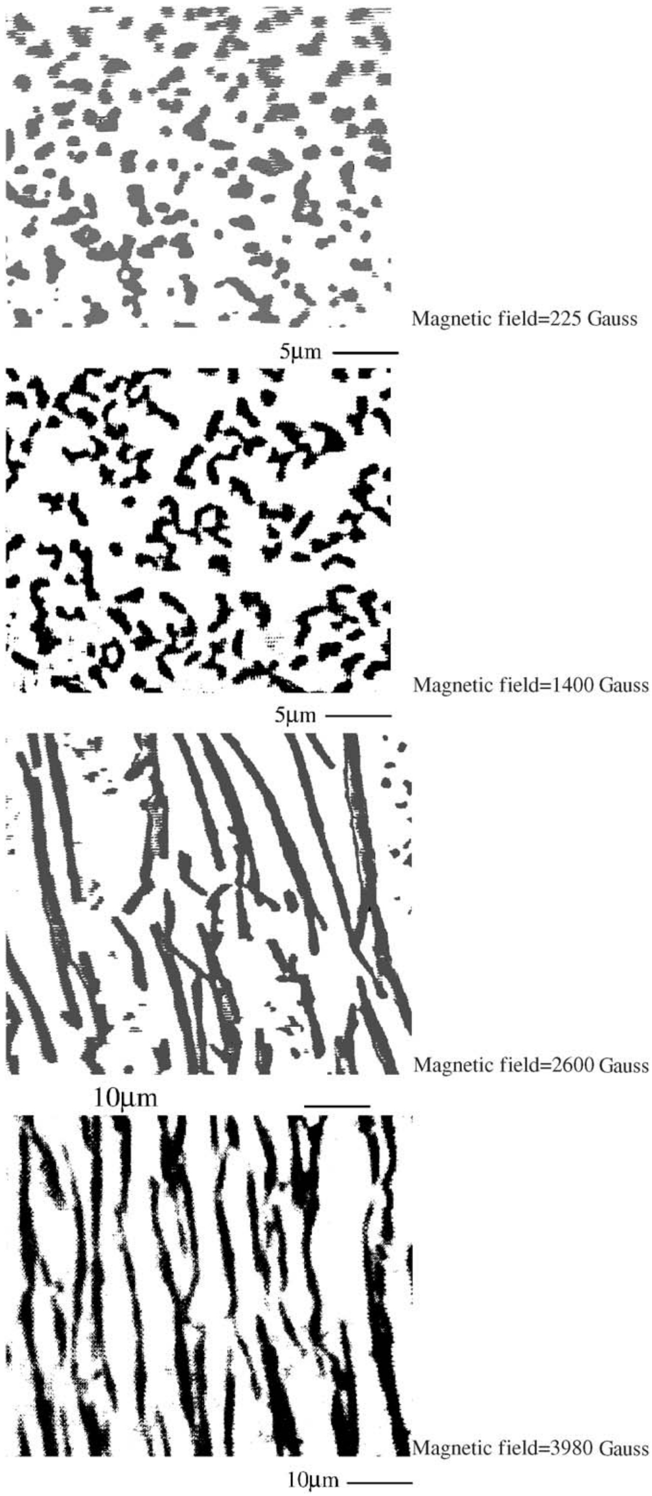

Fig. 9. (a–d) Photographs showing the chain formation ferrofluid films taken using CCD camera in different applied magnetic field values (sample $x = 0.1$).

$Zn_xFe_{1-x}Fe_2O_4$ which shows a linear decrease with the 'x' value in the series $Zn_xFe_{1-x}Fe_2O_4$ up to $x = 0.4$ and an abrupt change thereafter (Fig. 4). The saturating magnetic field values for the limiting output power for all the samples belonging to the series $Zn_xFe_{1-x}Fe_2O_4$ were also plotted against 'x' in the series. These results confirm the dependence of the limiting value of the transmission on the particle size.

These results indicate that the saturation field H_s for cluster formation in the series is determined by the particle size of these synthesized ferrofluids. From Fig. 6, it can be seen that the linear part in the graph can be employed to sense the magnetic fields and the maximum magnetic field that the film can sense is determined by the particle size. Also the broken clusters in high applied magnetic fields itself shows some inhomogeneities in the magnetic field distribution. If these clusters could be grown in a controlled magnetic field, in diluted ferrofluids, possibility of obtaining a magnetic field-controlled grating/system of narrow wires whose width and length could be controlled by the applied magnetic field, saturation magnetization and concentration of the samples.

4. Conclusion

Magnetic field-induced structural anisotropy is found to be responsible for the observed variation in the transmitted intensity of the ferrofluid samples. The limiting of the output intensity can be attributed to the saturation in the cluster formation and the anisotropy. The saturation of the cluster formation is verified experimentally by imaging them under different applied magnetic field. This limiting value is found to be dependent on the particle size and saturation magnetization of these samples. Also the broken clusters show small inhomogeneities in the magnetic fields. These findings give further scope for the application of ferrofluids in switching devices with limiting value of the output power tuned by the particle size and magnetization.

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