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Enhanced shape anisotropy and magneto-optical birefringence by high energy ball milling in $Ni_xFe_{1-x}Fe_2O_4$ ferrofluids

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Abstract

Ferrofluids belonging to the series $Ni_xFe_{1-x}Fe_2O_4$ were synthesised by two different procedures—one by standard co-precipitation techniques, the other by co-precipitation for synthesis of particles and dispersion aided by high-energy ball milling with a view to understand the effect of strain and size anisotropy on the magneto-optical properties of ferrofluids. The birefringence measurements were carried out using a standard ellipsometer. The birefringence signal obtained for chemically synthesised samples was satisfactorily fitted to the standard second Langevin function. The ball-milled ferrofluids showed a deviation and their birefringence was enhanced by an order. This large enhancement in the birefringence value cannot be attributed to the increase in grain size of the samples, considering that the grain sizes of sample synthesised by both modes are comparable; instead, it can be attributed to the lattice strain-induced shape anisotropy(oblation) arising from the high-energy ball-milling process. Thus magnetic-optical (MO) signals can be tuned by ball-milling process, which can find potential applications.

Keywords: Ferrofluid; Co-precipitation; HEBM; Birefringence

1. Introduction

Ferrofluids are stable colloidal suspensions of ultrafine single-domain magnetic nanoparticles having grain sizes of the order of 10 nm suspended in a chemically inert carrier liquid [1]. These ferrofluids can be either surfactant coated or ionic with particle density of the order of $10^{22}/m^3$. Surfactant coated ferrofluids are important both from the fundamental and from the technological point of view because of their excellent stability against agglomeration.

Extensive studies have been carried out in ferrofluids, especially in their optical magnetic and magneto-optical (MO) properties [2–6]. These include scattering, absorption and transmittance studies in which they show many peculiar properties because of the randomness in the medium. Their MO characterisation leads to understanding of many of their fundamental and transport properties in the presence of applied magnetic field.

Their MO properties include birefringence, dichroism, Faraday, Kerr and Cotton Mouton rotation, and ellipticity. It was Kerr (1901) and Cotton-Mouton (1907) who first observed this optical parameter variation in the magnetic materials in the presence of magnetic field. In the absence of an applied magnetic field these fluids behave like any other colloid and the application of magnetic field modifies the dynamic properties greatly. However there are reports suggesting that these samples exhibit zero-field birefringence and that dichroism [3] is present in these samples. However, no such observations were reported in case of surfacted ferrofluids.

Applications for birefringence are numerous and versatile. Birefringence is widely used in optical devices, such as liquid crystal displays, light modulators, colour filters, wave plates, optical axis gratings, etc. It also plays an important role in second-harmonic generation and many other nonlinear processes. It is also utilised in medical diagnostics. (Needle biopsy of suspected gouty joints will be negatively birefringent if urate crystals are present.)

Ferrofluids under the influence of a magnetic field induce MO anisotropy, and contribute to birefringence and

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dichroism [7]. In the magneto-transverse mode, the eigenmodes are linearly polarised waves, making the dependence quadratic in the presence of an applied magnetic field. The difference in speed and absorption gives rise to linear birefringence and dichroism. These properties dictate the usefulness of these materials for probable applications in devices such as light-intensity modulator, magnetic-field-controlled switches and magnetic-field-induced gratings [8].

In the present investigation, ferrofluid samples belonging to the series $Ni_xFe_{1-x}Fe_2O_4$ are synthesised both by the precipitation (and in situ surfactant coating) method and by high-energy ball-milling (HEBM) techniques. Their structural, magnetic and MO properties, namely birefringence and dichroism, are evaluated and the results are compared. The comparison of such a system for the present investigation helps to study the effect of anisotropy (which will be greater for the ferrofluids synthesised by HEBM) in shape and size on the MO properties. Attempts are made to explain the observed effects with a theoretical model. The effects of aggregation and shape anisotropy are also discussed.

2. Experimental techniques

2.1. Synthesis of ferrofluids

2.1.1. Co-precipitation method

Ferrofluids belonging to the series $Ni_xFe_{1-x}Fe_2O_4$ have been synthesised by the co-precipitation technique [9], with oleic acid as the surfactant. The obtained wet slurry was then successfully dispersed in kerosene with a known volume fraction to obtain ferrofluids of desired concentration.

2.1.2. High energy ball milling method (HEBM)

Fine magnetic particles were synthesised by the co-precipitation method and dried. The as prepared particles were then subjected to HEBM by employing Refs. [10,11].

2.2. X-ray diffraction studies

X-ray diffraction of the samples was recorded in an X–ray diffractometer (Rigaku Dmax-C) using Cu-Kα radiation ($\lambda = 1.5406$ Å) [11]. Lattice parameter (a) was calculated assuming cubic symmetry [12]. The average particle size of these powder samples was estimated by employing Debye Scherrer's formula.

2.3. Transmission electron microscopic studies

Grain size and morphological studies were carried out on a ball-milled fine particles system belonging to the series $Ni_xFe_{1-x}Fe_2O_4$ by the transmission electron microscopy method. The machine used was a JEOL (Tokyo, Japan) field emission TEM (FE-TEM) model 2010F with an operating voltage of 200 kV. Here, a dried ferrofluid specimen is irradiated with an electron beam of uniform current density. Electron diffraction spectrum is also recorded.

2.4. Vibrating sample magnetometry (VSM)

Magnetic characterisation of the ferrofluids belonging to the series $Ni_xFe_{1-x}Fe_2O_4$ was carried out by using vibrating sample magnetometry (VSM) (model: EG & G PAR 4500). The saturation magnetisation (M_s), retentivity (M_r) and coercivity (H_c) were measured at room temperature.

2.5. Set-up for the measurements of birefringence

Ferrofluids synthesised by both techniques are taken in sample cells of 1 mm thickness. The samples were diluted with the carrier (to known volume fraction) so as to minimise the dichroic effects, and the birefringence signal with normalised volume fraction was measured. The retardation is measured using a system including an analyser, Soleili Babinet compensator, photomultiplier tube (PMT) and oscilloscope mounted on an optical bench and the applied magnetic field direction is always kept transverse to the light propagation. A schematic of the set-up is shown in Fig. 1. The polarimetry used was fabricated with polarisers (high extinction coefficient), analysers, quarterwave plates etc.

The PMT used was shielded against the magnetic field as in any magneto-optical signal capturing. These details are included in the text as well. The ellipsometer was assembled using nicol polarisers (also an analyser which is again another polariser) and quarter wave plates.

Magneto birefringence data measured with a lock-in amplifier automated using LabVIEW software package are also provided.

Soleili Babinet compensator helps to have a direct measurement of the phase retardation of the perpendicular and parallel polarised waves. The phase retardation is also measured with the help of a lock-in amplifier (DSP 7260). Birefringence is calculated from the phase retardation.

$$\Delta n = \lambda\delta/2\pi l,$$

where 'δ' is the relative retardation of the components of light (directly measured with Babinet's compensator), λ the wavelength of light used and 'l' is the length of propagation of light through the sample, which is the thickness of the fluid film.

Birefringence is measured with different applied magnetic field values for the purely chemically synthesised as well as wet-milled samples. The same experimental set-up is employed to study the variation of birefringence with sample volume fraction also.

3. Results and discussions

The X-ray diffraction spectrum (Fig. 2) shows that the samples are almost phase pure, and estimation of the

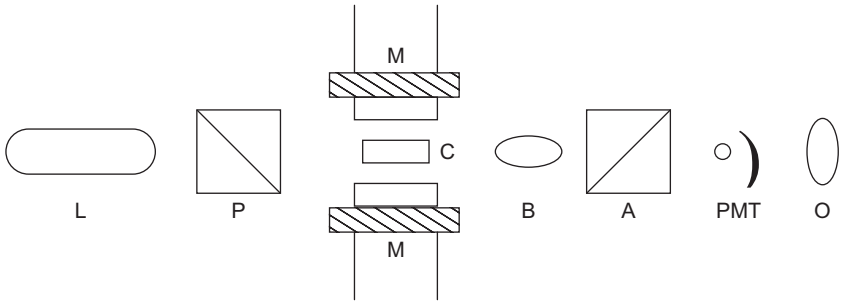

Fig. 1. Experimental set-up for linear birefringence. (L—laser, P—polariser, M—magnet, C—sample cell, B—babinet compensator, A—analyser, PMT—photomultiplier tube, and O—storage oscilloscope).

average grain size from the line broadening points to the fact that the particle size lies in the range 50–90 Å for all the chemically synthesised samples, which is also verified using TEM.

The lattice parameter is evaluated for all samples belonging to the series $Ni_xFe_{1-x}Fe_2O_4$, assuming cubic symmetry. The variation of lattice parameter with composition × (Fig. 3) is in accordance with the Vegards law [13]. However, the lattice appears to shrink in the case of ball-milled $Ni_xFe_{1-x}Fe_2O_4$ samples probably because of the high impact imparted to the fine powder samples during milling. The evaluation of structural parameters becomes important to understand the contribution of structural anisotropy (shape anisotropy) in the context of the magneto-optical properties exhibited by ferrofluids.

TEM images of the dried ferrofluids (synthesised by both methods) belonging to the series $Ni_xFe_{1-x}Fe_2O_4$ show that the particles are ultrafine with particle size varying from 60 to 100 Å. The electron diffractogram is also recorded and the planes were identified which matches well with the data obtained from the X-ray diffraction analysis. A typical TEM diffractogram is depicted in Fig. 4.

The magnetisation curves for the samples belonging to the series $Ni_xFe_{1-x}Fe_2O_4$ (Figs. 5 and 6) synthesised both by the precipitation method and by the ball-milling process agrees well with the magnetisation values predicted by Neel's Two sublattice model when plotted for normalised concentration (Fig. 7). The magnetisation values of these ferrofluids seems to be unaffected by the ball-milling process to an extent. However, there are reports of change in magnetisation during the HEBM process [14]. Such a remarkable change is not observed in this case, may be because of the lower milling time.

Their magneto-optical investigations show that the birefringence decreases in the series $Ni_xFe_{1-x}Fe_2O_4$ from $x = 0$ to 0.7 (Figs. 7 and 8).

The variation of birefringence signal (saturation value) is in accordance with the variation pattern of the magnetisation in the series $Ni_xFe_{1-x}Fe_2O_4$ for both chemically synthesised and ball-milled ferrofluids.

The application of magnetic field in these ferrofluids induces magneto-optical anisotropy, which mainly contributes to the birefringence and dichroism [5]. In the longitudinal configuration, in which the wave vector of the incident light is directed along the applied magnetic field,

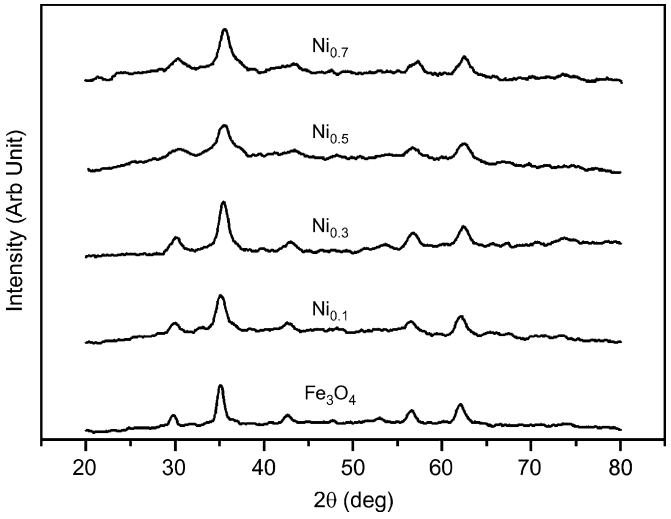

Fig. 2. XRD spectrum of ferrofluid samples $Ni_xFe_{1-x}Fe_2O_4$.

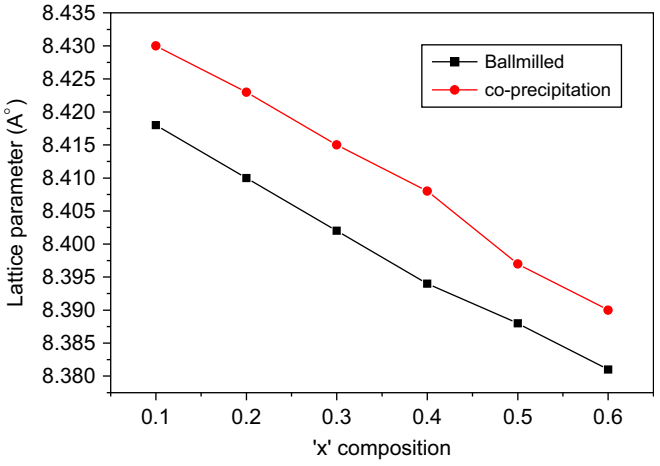

Fig. 3. Variation of lattice parameter with composition in chemically synthesised and ball-milled ferrofluids.

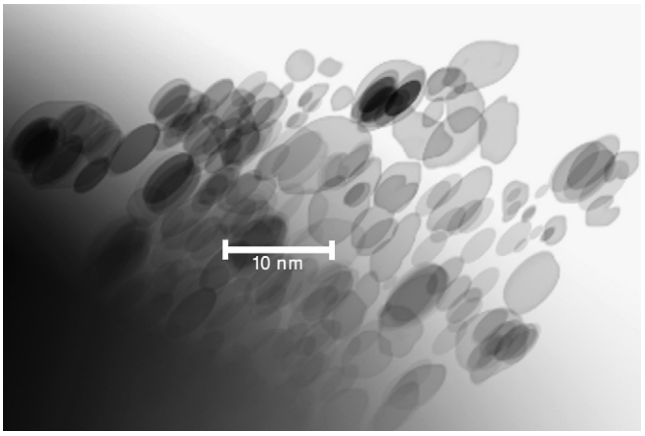

Fig. 4. TEM image of a representative ferrofluid sample (ball-milled).

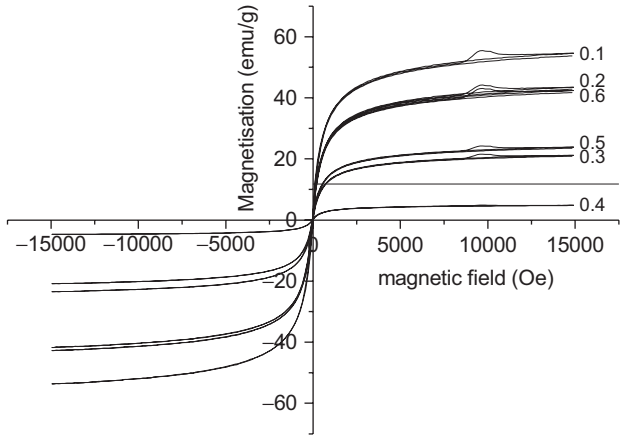

Fig. 5. Variation of magnetisation in the ferrofluid samples synthesised by HEBM (normalised volume fraction = 1 i.e., the precursor powder samples).

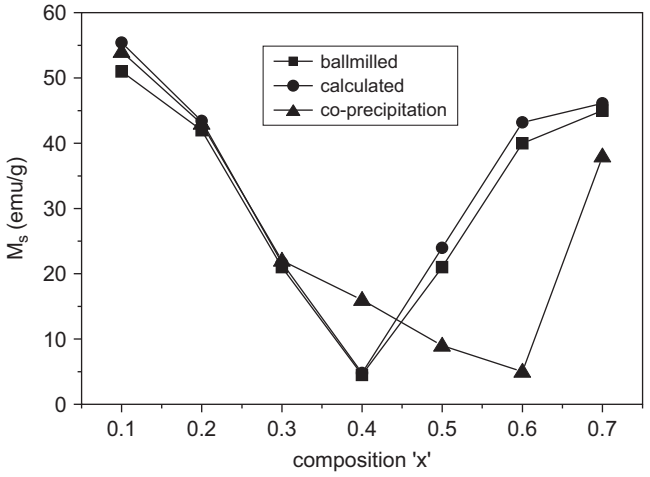

Fig. 6. Saturation magnetisation M_s (emu/g) vs. composition 'x' in $Ni_xFe_{1-x}Fe_2O_4$.

the eigenmodes of the electric field are circularly polarised waves [15]. The difference in speed and absorption of these waves induces circular birefringence and dichroism, which

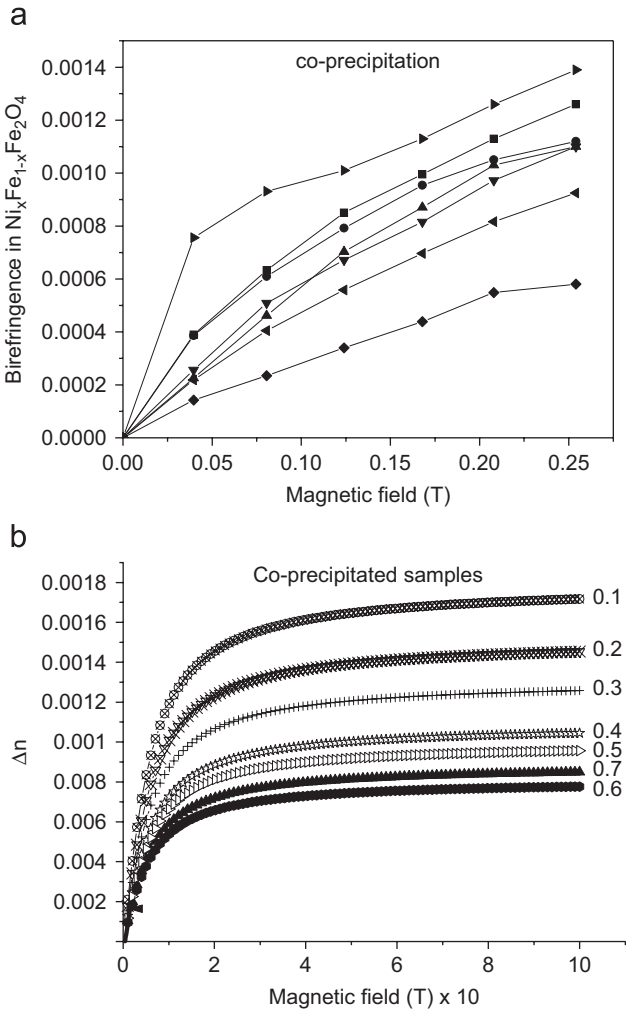

Fig. 7. (a) Birefringence in chemically synthesised ferrofluids (using optical methods). (b) Birefringence in chemically synthesised ferrofluids using lock-in amplifier (automated).

can be related to Faraday rotation and ellipticity, which are odd functions of magnetic field and are linear in magnetic field, while the birefringence and dichroism are quadratic in low applied magnetic fields, both proportional to the same Langevin function, as these effects are determined by transverse magnetic field [5].

In the magneto-transverse mode, the eigenmodes are linearly polarised waves, making the dependence quadratic in applied magnetic field. This gives rise to linear birefringence and dichroism. So the birefringence increases quadratically with applied magnetic field in the low-field regime.

The birefringence for a non-agglomerated ferrofluid can be fitted to the second Langevin's function

$$\Delta n_{\mathrm{ef}} = 1 - \frac{3}{A}\coth(A) + \frac{3}{A^2},$$

where, the quantity

$$A = (MVH/k\mathrm{T}),$$

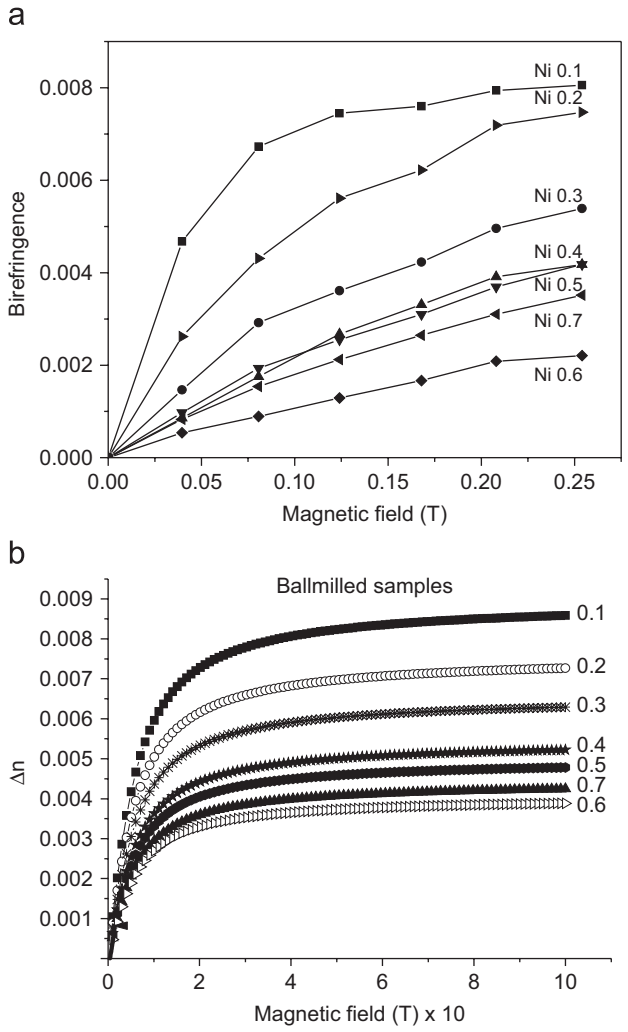

Fig. 8. (a) Birefringence in ball-milled ferrofluids using optical methods. (b) Birefringence in ball-milled ferrofluids using lock in amplifier (automated).

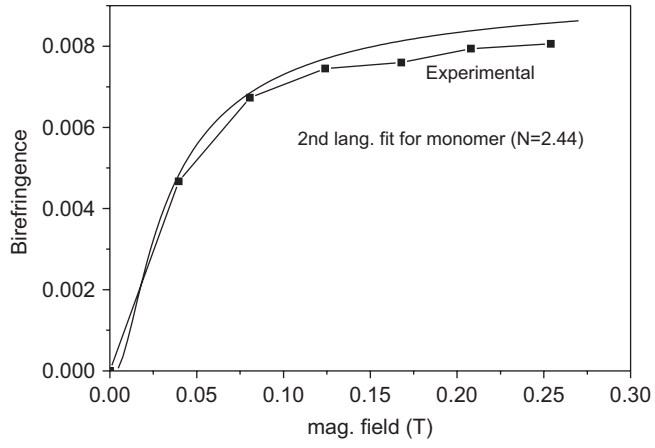

Fig. 9. Representative Langevin curve fitting and experimental birefringence values (fit for $N = 2.44$) for ball-millled $Ni_xFe_{1-x}Fe_2O_4$ ($x = 0.1$).

with $V = (\pi/6)D^3$, H is the magnetising field. Thus birefringence varies as H^2 in low applied magnetic field values, and in higher applied field values the value tends to saturate.

In a log-normal distribution function, with particle size = 70 Å, with $\sigma = 0.36$, the distribution function for the particle size can be written as

$$P(D) = \frac{\exp(2\sigma^2)}{D_{\text{avg}}\sqrt{2\pi}} \exp \frac{-\ln^2(D/D_{\text{avg}})}{2\sigma^2}.$$

Using the distribution function, the birefringence can be theoretically calculated using the second Langevin's function and the fit for monomer with the experimental result is given in Fig. 9, which is quite a good agreement for the co-precipitated ferrofluids.

From the TEM photographs (and also from the XRD studies), the average grain size is almost the same. However, due to the high shape anisotropy originating from the oblation, wrong answers will result when we try to substitute the average diameter in the calculation. The actual magneto-optical data are very high as compared to the calculated one. Rather, a fit for particles with double size as compared to the TEM gives good agreement. This shows the large shape anisotropy contribution to the signal, which makes it as big as that produced by particles with volume 2.5 times that of the spherical particles.

It was again expected that there can be pre-existing clusters in ball-milled samples. However, from the TEM measurements, it can be seen that the contribution is from the shape anisotropy rather than due to the aggregate formation.

Birefringence shown by ball-milled ferrofluids, however, does not agree with the monomer fit, and the fit for a dimer (for $N = 2.44$) is rather in good agreement with the experimental data in the case of ball-milled ferrofluids (Fig. 10).

Hence, it can be assumed that the shape and size anisotropy also play a bigger role in case of ball-milled ferrofluids. Also, it is assumed that the cluster formation is also higher in case of ball-milled ferrofluids and the fit for $N = 2.44$ is almost in agreement with the observed birefringent signal. The higher birefringent signal in the ball-milled

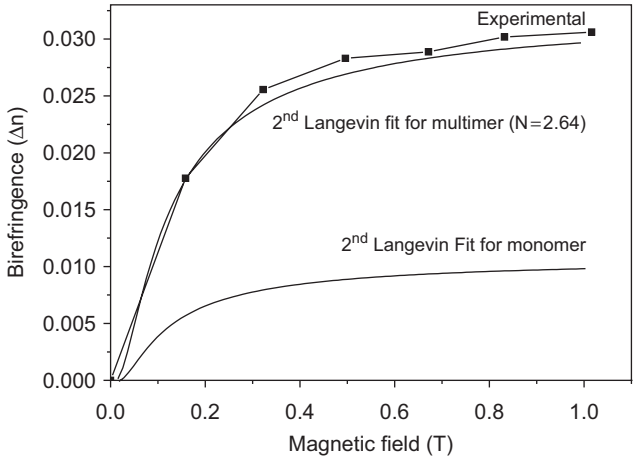

Fig. 10. Langevin curve fitting and experimental birefringence values (fit for multimer $N = 2.5$) for ball-milled $Ni_xFe_{1-x}Fe_2O_4$ ($x = 0.1$).

ferrofluids can also be attributed to the mechanical stress and strain imparted in the course of high-energy ball milling, which enhances the shape anisotropy, thereby enhancing the birefringent signal in addition to the dimer formation. So it can be concluded that the birefringent signal gets modified by the high energy ball-milling process.

An anomalously strong magneto-optical effect is obtained for a magnetic fluid thin film subjected to 15 min of HEBM when an external magnetic field is applied in the direction perpendicular to the propagation of the light beam, thus making the magnetic fluid thin film possess a birefringent property. In consequence thereof, a phase difference appears between the two modes of light which pass through the magnetic fluid thin film. The phase difference is a single-valued function of the magnetic field applied to the thin film. An apparatus using such an effect (hereinafter referred to as magnetic fluid thin film's anomalous pseudo-cotton-mouton effect) is primarily used for detecting a magnetic field and can be used as a magnetic field sensor, a transformer, an apparatus for controlling light intensity containing an optical shutter and an optical modulator, an optically bistable apparatus, a memory for an optical computer, a light-intensity stabiliser for lasers and an optical amplifier.

Furthermore, if birefringence could be controlled by the magnetic field, the application is still higher. Here, inducing shape anisotropy by small milling times induces a higher magneto-birefringence. Hence, without synthesising another set of samples, and spending time for the study of their composition, a material with higher magneto-birefringence can quickly be synthesised just by 15 min ball milling.

4. Conclusion

$Ni_xFe_{1-x}Fe_2O_4$ ferrofluids were synthesised by two different methods to study the effect of attrition on their magneto-optical signals. The birefringence measurements on chemically synthesised samples were satisfactorily fitted to the standard second Langevin's function for identical spherical particles. The magneto-optical signals obtained from ball-milled ferrofluids show that the assumption of a "system of identical spherical particles" fails. Size and shape anisotropy enhancement resulting from the ball-milling process results in the enhanced birefringent signal. The aspect ratio (length/breadth ratio) is calculated theoretically from the birefringent signal. This large enhancement in birefringence signal by simple ball milling for a short span can find enormous application potential as the MO signals can be tuned by high-energy ball milling.

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