IOP PUBLISHING NANOTECHNOLOGY

Nanotechnology **22** (2011) 375702 (7pp) doi:10.1088/0957-4484/22/37/375702

Nonlinear and magneto-optical transmission studies on magnetic nanofluids of non-interacting metallic nickel nanoparticles

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Received 5 March 2011, in final form 9 July 2011
Published 19 August 2011
Online at stacks.iop.org/Nano/22/375702

Abstract

Oxide free stable metallic nanofluids have the potential for various applications such as in thermal management and inkjet printing apart from being a candidate system for fundamental studies. A stable suspension of nickel nanoparticles of ∼5 nm size has been realized by a modified two-step synthesis route. Structural characterization by x-ray diffraction and transmission electron microscopy shows that the nanoparticles are metallic and are phase pure. The nanoparticles exhibited superparamagnetic properties. The magneto-optical transmission properties of the nickel nanofluid (Ni-F) were investigated by linear optical dichroism measurements. The magnetic field dependent light transmission studies exhibited a polarization dependent optical absorption, known as optical dichroism, indicating that the nanoparticles suspended in the fluid are non-interacting and superparamagnetic in nature. The nonlinear optical limiting properties of Ni-F under high input optical fluence were then analyzed by an open aperture z-scan technique. The Ni-F exhibits a saturable absorption at moderate laser intensities while effective two-photon absorption is evident at higher intensities. The Ni-F appears to be a unique material for various optical devices such as field modulated gratings and optical switches which can be controlled by an external magnetic field.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetic nanofluids are magnetic nanoparticles suspended in a carrier fluid. They find immense applications in heat transfer fluids, seals, sensors, loudspeakers, pigments and magnetic inks owing to a multitude of properties exhibited by them [1, 2]. The fabrication of stable metallic ferrofluids constituting atomic clusters of few hundreds of atoms is a hot topic of research. The size constraints of the nanoparticles result in modified electric, magnetic and optical properties with respect to their bulk counterparts [3–6]. The finite size results in a blue shift in semiconductors because of excitonic confinement. The ferromagnetic–antiferromagnetic multilayer and ferromagnetic composites exhibit spin polarized tunneling and tunneling magneto-resistance and these phenomena are exploited for sensing and data storage applications [3]. The magnetic nanoparticles exist as single domain which is a result of the interplay of domain wall energy and magneto-static energy. The magneto-crystalline anisotropy energy depends on the volume of the particle, and, below a critical size, the thermal energy can fluctuate the moments and cause spontaneous moment reversal as the paramagnetic moment relaxes. In a suspension of ferromagnetic nanoparticles, the Brownian motion of the particles will pose extended and interesting properties and their study is important from a fundamental perspective.

When the anisotropy of the nanoparticles is greater than the thermal energy, free relaxation of the particle moment (Neel type relaxation) in an external magnetic field does not occur. Under such circumstances the particle as a whole rotates so as to align the easy axis in the magnetic field direction. The complex magnetic characteristics of nanofluids are attributed to both Brownian and Neel relaxation mechanisms [1, 2]. The overall magnetic response of a nanoparticle suspended system depends on the particle properties, as well as the inter-particle interaction and the nature of the suspended medium. Nickel nanoparticles are widely used in industry because of their excellent catalytic activity. Nickel is a versatile catalyst for the cracking of methane to carbon nanotubes and hydrogen, partial oxidation, and steam reforming [7]. Nickel fluids with superparamagnetic fine particles behave as Newtonian fluids [7] and their synthesis and characterization are quite challenging and assume importance commercially.

Nonlinear optical materials with high order nonlinearity and fast response are much sought after technologically. The drastic advancement in the field of ultrafast and high intense lasers in research and technology demands protection for human eyes and sensitive optical devices. An ideal optical limiter is transparent at low fluences and opaque above a threshold intensity. However, practical optical limiters obey one or more nonlinear mechanisms which add up to give considerable nonlinear limiting nature. Control of the nonlinear properties via an external stimulus presents tremendous applications. The theoretical evaluation of such an externally controllable nonlinear optical material showed that the nonlinear character could be tuned by an external magnetic field [8]. Ferrofluids of iron oxide nanoparticles are known for their optical limiting property and have been studied by several researchers [9, 10]. Besides being magnetic in nature, these nanoparticles form complex microstructures under an applied external magnetic field and this could also tune their optical properties. The linear optical absorption and refraction properties are observed to vary with magnetic field [11, 12] and are explained as a result of the magnetic moment interacting with the electric field of radiation. In fluids, the inter-particle interactions depend on the magnetic property of the constituent particles and their surface chemistry can lead to the formation of mesoscopic chain like structures [13]. These field dependent aggregations modulate the transmitted intensity. Ferrofluids are potential field modulated gratings, fiber modulators [14, 15] and optical switches for optical technology. Magneto-optical measurements on the nanofluid can be employed to characterize the fluids and can be used to investigate the field induced aggregation [16] and the nature of interaction among the suspended particles.

A material whose nonlinear response can be tailored by application of an external magnetic field is of great interest to the technological world. Such a system requires an interaction between the magnetic susceptibility and nonlinear absorption of the material. Heterostructures or composites with a magnetic particle and nonlinear optical materials [17, 18] have been investigated with a view toward realizing magneto-controlled nonlinear optical materials for photonic devices. It is all the more convenient and simple if a magnetic material itself is nonlinear in nature. Ferrofluids with suspended nanoparticles having appropriate dimension are good candidates for such applications. Ferrofluids based on iron oxide and its derivatives [9] and one-dimensional metallic systems of cobalt [19] are reported to have optical limiting behavior.

The large surface to volume ratio of nanoparticles makes the synthesis of metallic systems difficult since they are highly prone to oxidation. The oxide layer modifies the magnetic properties, since the oxide of nickel is antiferromagnetic in nature. There are different routes for the synthesis of nickel nanoparticles, such as arc melting submerged in solvent, solution phase chemical reduction, thermal decomposition from organometallics [7, 20–23], etc. However, their dispersion in a suitable solvent and the stability of the resulting fluid are still a challenge on the ground. It is in this context that the synthesis of Ni nanofluids assumes importance. Nickel fluids are metallic in nature and resemble colloids of noble metals like gold and silver. Nanogold and nanosilver embedded in various matrices are important from an optical limiting point view and hence the nonlinear properties of Ni nanofluids are also important. Moreover, nickel, being magnetic and conducting the influence of the field assisted optical tuning, is another possibility. In optical limiting, agglomeration, chain formation and clustering also manipulate the overall limiting capability. Hence field induced optical transmission characteristics are necessary in order to verify whether they are non-interacting while in fluid. A survey of the literature reveals that there exist no simple techniques to synthesize phase pure Ni ferrofluids, nor are there are any reports on their nonlinear optical properties. Hence the primary motive of the present investigation is to synthesize phase pure Ni fluids and then carry out nonlinear optical studies. A study using field induced dichroism is necessary to ascertain whether the particles are interacting or non-interacting.

2. Experimental details

2.1. Synthesis of Ni nanofluid

Stable magnetic fluids of nickel were synthesized by high energy ball milling (HEBM) (Fritsch Pulverisette 7) of nanoparticles prepared by a modified sol–gel auto combustion technique. The synthesis of nickel nanoparticles is reported in detail elsewhere [24]. The particles are subjected to HEBM in the presence of surfactant oleic acid in water medium for 30 min at a speed of 500 rpm. The size of the particles is reduced considerably while milling. They are also peptized with oleic acid during the milling process. The sample is then retrieved and stirred in an almost neutral medium

(7.5 pH) at warm conditions (∼40 °C). The uncoated and larger sized particles are magnetically decanted. The residue containing coated particles is dried by adding acetone and finally dispersed in kerosene aided by ultrasonic agitation.

2.2. Characterization techniques

The structural characterization was carried out by the x-ray diffraction technique (Rigaku D Max C2) at a wavelength of Cu Kα. Transmission electron microscopy (TEM) was employed to determine the particle size and distribution, in a standard (JEM 2100F TEM) instrument. High resolution TEM (HRTEM)(JEM 2100F TEM) measurements were taken to confirm the crystal structure and to determine the phase purity of the Ni nanoparticles. In addition, micro-Raman studies were also performed at an excitation of 633 nm. The magnetic measurements were carried out in a superconducting quantum interference device (SQUID-MPMS Quantum Design). A UV–vis NIR spectrophotometer (Jasco-470) was used to measure the optical absorption in the visible and ultraviolet wavelengths. The input laser fluence dependent transmittance studies were carried out using an open aperture z-scan technique. The second harmonic output (532 nm) from a Q-switched Nd:YAG laser (Minilite, Continuum Inc.) was used for the measurements. The nominal pulsewidth of the laser was 5 ns. The fluid was taken in a 1 mm cuvette and the linear transmission of the samples at the excitation wavelength was adjusted to be 60%. The measurements were carried out at two laser pulse energies, namely 50 and 200 μJ. The magneto-optical dichroism measurements were carried out in an experimental set up designed in the laboratory. A low power (3 mW) 670 nm diode laser is incident on fluid taken in a sample cell of 1 cm × 1 cm, with the light incident normal to the applied field direction. The linear transmittance is fixed at 20%. The laser chopped by a mechanical chopper is incident through a polarizer on the sample placed between the pole parts of an electromagnet. The transmitted light is converged by a convex lens that collects all the light transmitted through the sample at the photodiode detector. A lock-in-amplifier detects the signal corresponding to chopping frequency alone so that the background noise is eliminated.

3. Results and discussion

The obtained fluid is highly stable against sedimentation under gravitational and moderate magnetic fields (5000 Oe). The x-ray diffraction pattern of the as prepared sample is depicted in figure 1. This indicates that Ni has crystallized in the face centered cubic phase (ICDD: 04 0850). The morphology and particle size were evaluated by transmission electron microscopy and are shown in figure 2(a).

The TEM image clearly shows that the suspended particles are uniform in size with an average diameter of 4–5 nm. The inset shows the size distribution. High resolution TEM studies were carried out on the Ni-F after drying and are shown in figure 2(b). The phase pure Ni nanoparticles can be clearly seen in the picture and any kind of oxide hull is also absent indicating that the Ni-F is oxide free. To further prove the oxide free nature of Ni-F, a micro-Raman study was carried out at 633 nm and is depicted in figure 2(c); the spectrum is devoid of any signature corresponding nickel oxide.

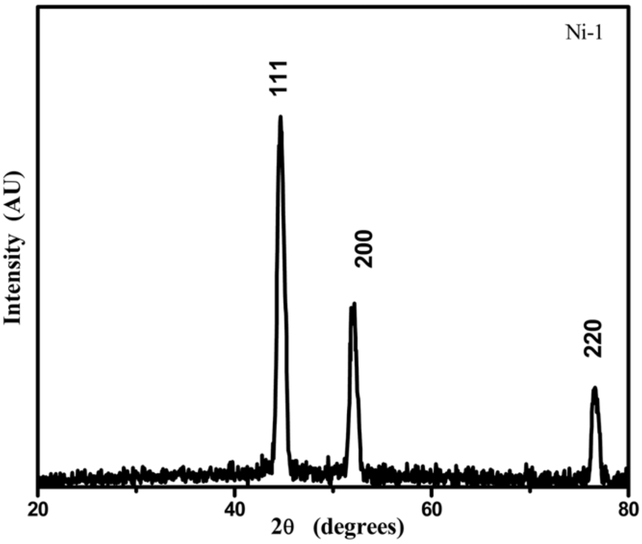

Figure 1. X-ray diffraction pattern of the Ni particles.

The magnetic measurements are indicative of the fact that the fluid particles are superparamagnetic in nature with zero remanence and zero coercivity. The $M(H)$ hysteresis loop is depicted in figure 3. The magnetization does not saturate even at high applied magnetic fields. This is to be expected from magnetic nanoparticles of a size of a few nanometers due to the large surface to volume ratios. The surface spins can be canted or frozen in random directions resulting in a paramagnetic behavior. This is the reason for the unsaturated $M(H)$ curve even with very high applied magnetic fields. The inset to figure 3 confirms that the particles are superparamagnetic in nature.

Figure 4 depicts the results obtained from open aperture z-scan measurements. The z-scan curves indicate the presence of two competing mechanisms in Ni-F at two different laser fluences. The results show saturable absorption behavior at moderate laser energies and an optical limiting behavior at higher energies.

The saturation trend is clearly visible in the z-scan curve corresponding to 50 μJ and optical limiting is clearly evident in the z-scan curve corresponding to 200 μJ (figure 6). This implies that there are two predominant causes for the nonlinearity: one is a saturation of the ground state absorption, and the other is an absorption by the excited state. In order to reach a meaningful conclusion on the nonlinear optical properties, linear absorption studies should be performed. The linear optical absorption measurements on the fluid show metallic nature with absorption increasing with photon energy (figure 5).

The linear absorption data can be correlated with the nonlinear properties. At the excitation wavelength of 532 nm the sample has a certain absorption (as it is evident from figure 5), whereas at the corresponding two-photon wavelength of 266 nm the sample shows relatively greater absorption

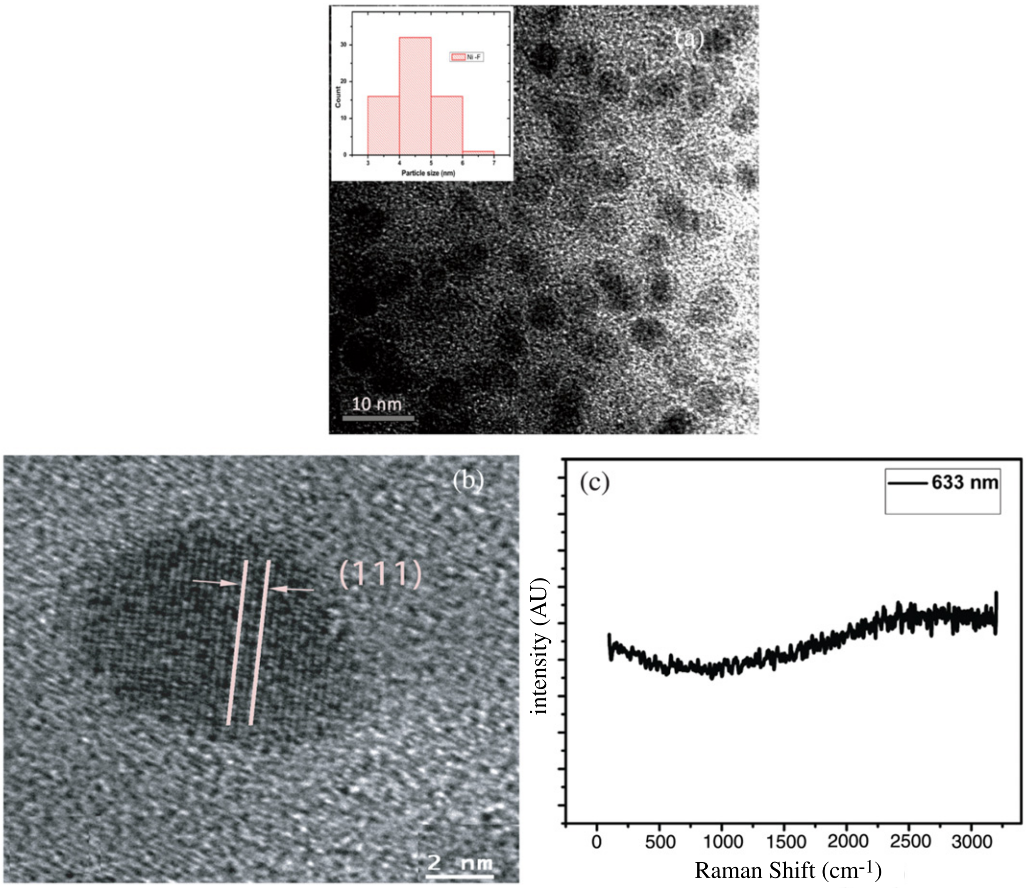

Figure 2. (a) TEM of the prepared Ni particles (inset showing the distribution histogram), (b) high resolution TEM and (c) micro-Raman spectrum of the Ni-F particles.

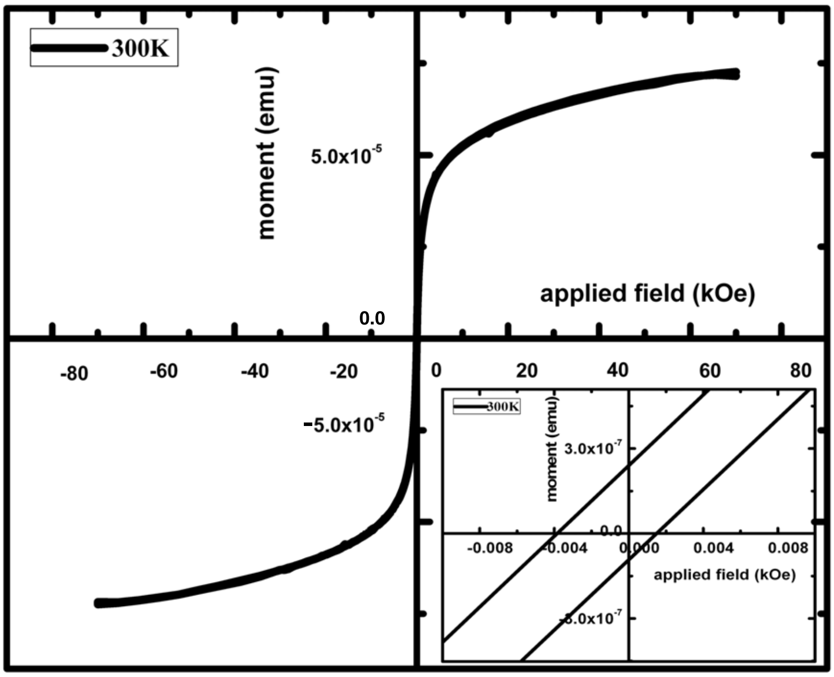

Figure 3. Hysteresis of the Ni particles at room temperature. Inset: closer look at low applied field.

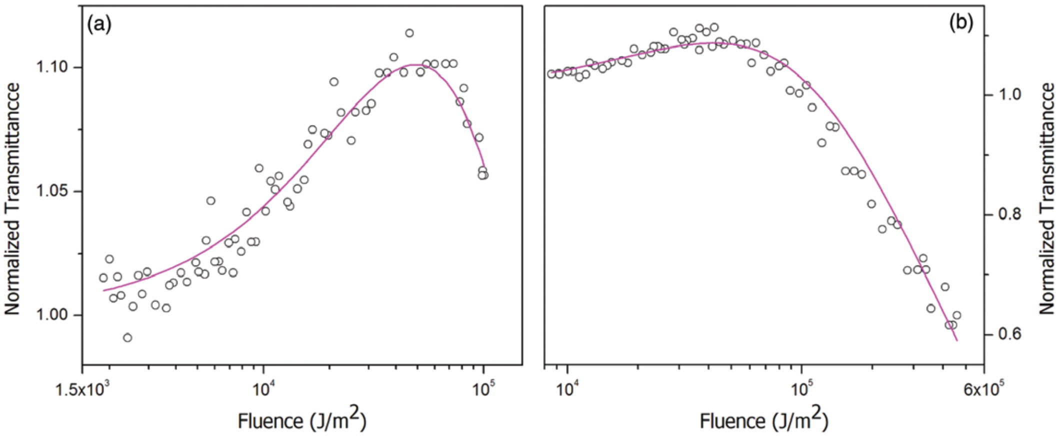

Figure 4. Fluence curves derived from the z-scan measurements for input laser energies of (a) 50 μJ and (b) 200 μJ. The circles are data points and the solid curves are numerical fits to the data using equations (1) and (2).

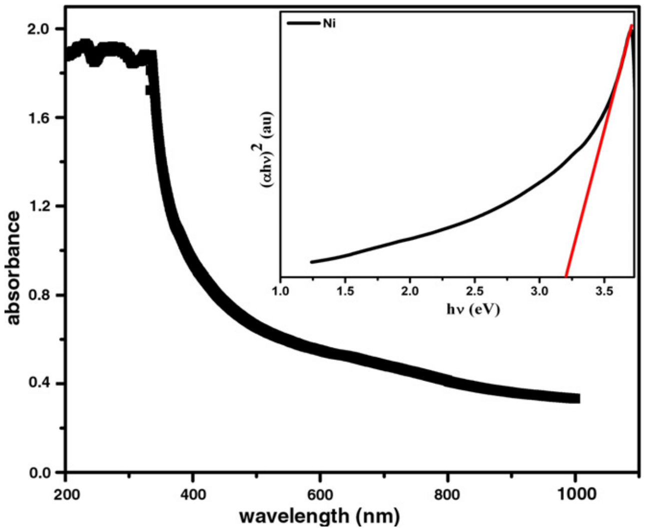

Figure 5. Optical absorption spectrum of the Ni fluid. The inset shows the Tauc plot for band gap calculation.

(figure 5). This indicates the existence of excited states suitable for two-step as well as genuine two-photon absorption processes. Therefore, an effective nonlinear absorption coefficient $\alpha(I)$, given by

$$\alpha(I) = \frac{\alpha_0}{1 + (\frac{I}{I_s})} + \beta I, \tag{1}$$

can be considered for modeling the z-scan results. Here α_0 is the unsaturated linear absorption coefficient at the excitation wavelength, I is the input laser intensity, and I_s is the saturation intensity. $\beta I = \sigma N(I)$ is the excited state absorption (ESA) coefficient, where σ is the ESA cross section and $N(I)$ is the intensity dependent excited state population density. The effect of genuine two-photon absorption is neglected because it will be much weaker compared to that of ESA. To calculate the transmitted intensity for a given input intensity, the propagation equation,

$$\frac{\mathrm{d}I}{\mathrm{d}z'} = -\left[\left(\alpha_0 \Big/ \left(1 + \frac{I}{I_s}\right)\right) + \beta I\right] I, \tag{2}$$

is numerically solved. Here z' indicates the propagation distance within the sample. By determining the best-fit curves for the experimental data, the nonlinear parameters are calculated.

I_s is found to be of the order of 10^{13} W m^{-2} and β is of the order of 10^{-11} m W^{-1}. For comparison, this β value is in the same range as those of copper nanocomposite glasses [25],

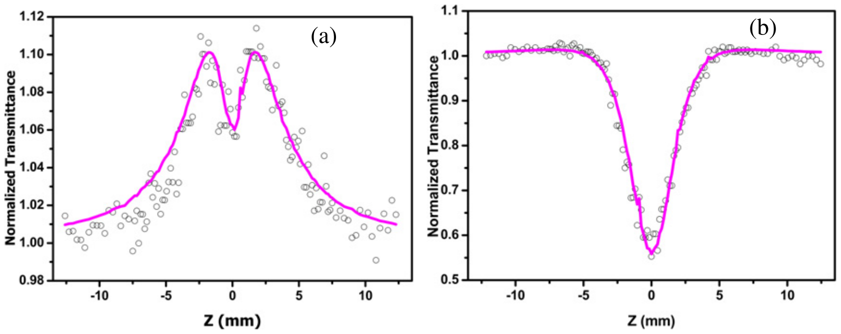

Figure 6. Z-scan curve corresponding to input energies of (a) 50 μJ and (b) 200 μJ. The hollow circles are data points and the solid curve corresponds to the numerical fit to the data using equation (2).

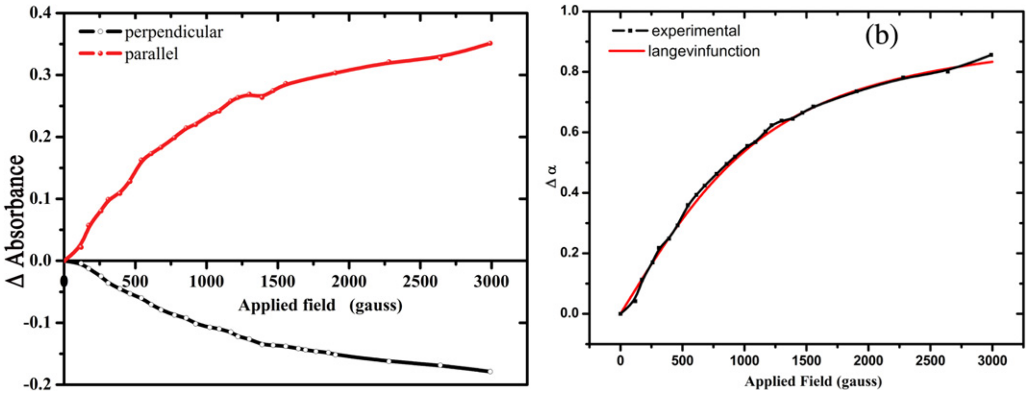

Figure 7. Magneto-optical dichroism in the nickel fluid: (a) absorbance for parallel and perpendicular polarizations and (b) difference in absorbance as a function of applied field.

bismuth nanorods [26] and conjugate polymer molecules [27], measured under similar experimental conditions. So the material under study is a good nonlinear optical material comparable to well known optical limiters with an added magnetic leverage.

The stability and particle agglomeration studies were conducted using linear magneto-optical dichroism measurements [28]. Dichroism refers to the differential absorbance of parallel and perpendicular polarized light through a medium. Generally magneto-optical effects in magnetic fluids are believed to be the consequences of anisotropy in dielectric constants induced by the orientation of the suspended particles. When the particles form chains in the direction of an applied magnetic field a kind of mechanical anisotropy is induced. This induced anisotropy results in optical anisotropy in the refractive index, in the absorbance, or in both. The orientation of the particles is either by motion of particles in the fluid or by the rotation of the particles that makes the moment align along the magnetic field direction. This is achieved by Neel relaxation or Brownian relaxation or a combination of them. The dichroism can result from anisotropic absorption or anisotropic scattering. In the case of field induced dichroism, the anisotropy vanishes as soon as the field is removed. Any remanence may result from the inter-particle interaction that causes the agglomeration of particles. Hence field induced dichroism measurements are vital to delve into the relaxation mechanism, field induced clustering, and chain formation.

The absorption as a function of applied field is measured in transverse mode with the polarization of the incident light parallel and perpendicular to the applied magnetic field direction. The differential absorption for both parallel and perpendicular polarized light with respect to the field direction is depicted in figure 7. The fluid exhibits the exact intrinsic dichroism reported [28, 29]:

$$\Delta A_{\text{parallel}} = -2\Delta A_{\text{perpendicular}}.$$

It may be noted that the intensity regains the zero field value as the field is removed in either polarization. This indicates that the particles are superparamagnetic with least particle agglomeration. The anisotropy as a function of applied field is presented in figure 7(b). It is seen that the differential absorbance follows Langevin type behavior as modeled [30] earlier. This behavior is for independent particle orientation forming a one-dimensional chain without any interaction of adjacent chains. The rapid relaxation of the optical transmission points out that the field induced aggregates are short lived with smaller dimensions [31], which happens when the interaction of the particles with the applied field has greater strength than the inter-particle interaction.

The field and fluence dependent light transmission properties of this particular metallic nanofluid indicate that they are unique for various photonic applications. Aside from their huge industrial applications such as in thermal management, they can even find applications in selective photon absorption and fluid based polarizers.

4. Conclusions

Stable magnetic nanofluids of metallic nickel nanoparticles have been synthesized by a two-step route. Structural analysis by x-ray diffraction, micro-Raman studies and TEM shows that the suspended particles in the nanofluid are nanocrystalline with pure metallic phase. Nonlinear optical studies by open aperture z-scan exhibit the presence of absorption saturation and excited state absorption. The field induced dichroism measurements reveal the non-interacting nature of the constituent particles which are superparamagnetic. This fluid can make magnetic field controllable optical gratings, and could be a potential magnetically modulated nonlinear material, since the constituent particles align in an external magnetic field and become suddenly randomized when the field is removed retaining their fluid nature.

Acknowledgments

MRA acknowledges the AICTE sponsored project 'Center for ferrofluids' and the DST DAAD exchange programme. RMAP thanks CSIR for a fellowship. The authors are grateful to Professor Manfred and Dr Denis Makarov of the Technical University Chemnitz, Germany for TEM measurements.

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