Optical Nonlinearity in NiFe$_2$O$_4$ Nanoparticles

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Nanocrystalline NiFe$_2$O$_4$ (Nickel Ferrite) particles were synthesized using the coprecipitation technique and subsequently their nonlinear optical properties were studied using the open aperture Z-Scan experiment employing nanosecond and femtosecond laser pulses. A significant optical limiting is observed in both cases showing that NiFe$_2$O$_4$ is a potential optical limiter having a broad temporal response, useful for device applications.

Key words: Optical limiting, Nickel Ferrite Nanoparticles, Optical nonlinearity, z-scan, three-photon absorption.

1. INTRODUCTION

The field of Nanoscience and Technology has been growing rapidly in the past few years since the realization of the fact that creating new materials and devices from Nanoscale building blocks could pave the way for accessing new and improved properties and functionalities. Ferrites are among the most widely used electromagnetic materials for a broad category of applications over a wide frequency range, due to their low cost and high performance\textsuperscript{[1]}. The unique electronic and physical structure\textsuperscript{[2]} of ferrites lead to several applications. Ferrites are used as high-frequency magnetic materials with their high electrical resistivity, and in the nanoscale regime they can act as low-loss materials at very high frequencies. They also find applications in electronics;\textsuperscript{[3]} as ferrofluids;\textsuperscript{[6]} in catalysis\textsuperscript{[7]} due to their easy separation and reusability; and in gas sensors due to their high sensitivity toward reducing gases such as liquefied petroleum gas (LPG), H$_2$S, etc. even at very low operating temperatures.\textsuperscript{[8],[9]} Nanomagnetic ferrite particles also find applications in the field of medicine as MRI contrasting agents\textsuperscript{[10],[11]} and in drug delivery systems.\textsuperscript{[13],[14]} Although the magnetic property of NiFe$_2$O$_4$ has been widely studied, till date the optical limiting studies have not been carried out. Hence in this paper we report experimental investigations of the third order optical nonlinearity of NiFe$_2$O$_4$ nanoparticles synthesized using the coprecipitation technique, employing the Z-scan technique.

2. EXPERIMENTAL

Chemicals (AR grade): NiCl$_2$.6H$_2$O, FeCl$_3$ (anhydrous), and NaOH pellets were purchased from CDH chemicals (India) and were used without further purification. The molar ratio between the initial precursors for the formation of NiFe$_2$O$_4$ is 1:2:8. In a typical synthesis procedure, 1.19 g (0.05M) of NiCl$_2$.6H$_2$O and 1.62 g (0.1M) of FeCl$_3$ were dissolved in 100ml of deionized water. The reaction mixture was stirred vigorously at 100°C and at this juncture 1.6 g (0.4M) of NaOH was added and a precipitate was formed. The solution was allowed to cool down and the particles were repeatedly washed using ethanol and deionized water for obtaining high purity. The precursors were obtained by evaporating the solution on a hot plate at 100°C. The dried precursor was crushed into a powder using a mortar and pestle.

The product was characterized for crystal phase identification by powder XRD using a D8 Advanced diffractometer (Bruker, Germany) with Cu Kα1 radiation with an X-ray wavelength of 1.5406 Å. Infrared Spectra of the powders (as pellets in KBr) were recorded using a Fourier Transform Infrared (FT-IR) Spectrometer (Thermo Nicolet, Avatar 370) in the spectral range of 4000 - 400 cm$^{-1}$ and with resolution of 0.9 - 1 cm$^{-1}$. The morphology of particles was studied by Scanning Electron Microscopy (JEOL, JSM - 6390LV) at 30 kV. EDAX analysis was conducted on an Energy dispersive x-ray spectrometer (JEOL, JED – 2300) attached to the Scanning Electron Microscope using which the compositional analysis was done.

The optical nonlinearity measurements were carried out using laser pulses of 5 ns ($\lambda$=532 nm, Nd: YAG laser) and 100 fs ($\lambda$=800 nm, Ti: Sapphire laser) durations (FWHM). The technique of open aperture Z-scan was used which gives information on the nonlinear absorption of the sample. In the Z-scan experiment, a laser beam is first focused using a lens, and the direction of beam propagation is taken as the z-axis. The focal point is considered as $z=0$. The z-value increases toward either side of the focal point, but the sign will be negative on one side and positive on the other (similar to a number line). The sample is now placed in the beam at a position ($z$) between the lens and the focal point, and the transmitted energy is measured.
Then the sample is moved in small steps toward the focus and beyond, and the transmission is measured at each step. At each of these positions, the sample will experience a different laser intensity, and the intensity will be a maximum at the focus. Thus in practice the open aperture Z-scan is essentially a sample transmission measurement, the data being continuously taken while the sample is slowly translated from a position before the focus to a position after the focus. If a spatially Gaussian laser beam is used, then each z-position will correspond to an input laser energy density (fluence) of \( 4(\ln 2)^{1/2}E_{in}/\pi^{1/2}o(z)^{3/2} \), where \( E_{in} \) is the input laser pulse energy and \( o(z) \) is the beam radius. \( o(z) \) is given by \( o(0)[1+(z/z_0)^2]^{1/2} \), where \( o(0) \) is the beam radius at the focus and \( z_0 = \pi o(0)^2/\lambda \) is the Rayleigh range (diffraction length), where \( \lambda \) is the excitation wavelength. Thus from the open aperture Z-scan data, it is possible to draw a graph between the input laser fluence and the sample transmission. The nature of this graph will reveal the sign and magnitude of the absorptive nonlinearity of the system.

In our experiment a planoconvex lens of 20 cm focal length was used to focus the laser, and the focal spot radius was about 18 µm. The samples were measured at three different laser pulse energies of 100, 200 and 300 µJ. Sample solutions were taken in a 1 mm thick glass cuvette (Hellma GmbH) and mounted on a programmable linear translation stage. The input energy reaching the sample and the energy transmitted by the sample were measured using two pyroelectric energy probes (RjP 735, Laser Probe Inc.). The interval between successive laser pulses was kept sufficiently large (about 1 s) to allow for complete thermal relaxation of the sample between adjacent laser pulses. The whole experiment was automated using a PC.

RESULTS AND DISCUSSION

The XRD pattern of the NiFe₂O₄ sample is shown in Figure 1. The peaks obtained were identified using the JCPDS (Joint Committee on Powder Diffraction Standards) tables and they are similar to the report given earlier by Zhou et al.¹⁵. The average particle size of the powder sample was estimated using the Debye Scherrer’s formula \( D=0.9\lambda/(\beta \cos\theta) \), where \( \lambda \) is the wavelength of the X-ray radiation, \( \beta \) is the full width at half maximum (FWHM) of the XRD peak with highest intensity, \( \theta \) is the diffracting angle and \( D \) is the particle diameter. The mean particle diameter ranged between 50-60 nm.

The FTIR spectra of nanocrystalline NiFe₂O₄ is shown in Figure 2. The broad band at ~3500 cm⁻¹ and the short band at ~ 1630 cm⁻¹ are caused by the O-H stretching vibrations interacting through H bonds. Traces of CO₂ are evident by the peak at 2350 cm⁻¹. Similarly the metal-oxygen bands were also observed in the range of ~ 1000 – 400 cm⁻¹. The spectrum we obtained is similar to that reported before [16]. The morphology of NiFe₂O₄ powders was investigated by Scanning Electron Microscopy and the compositional analysis of the samples was done through the Energy dispersive x-ray analysis (EDAX). The SEM images (Figure 3) clearly show the presence of spherical and rod shaped particles.
From the EDAX spectrum (Figure 4), it was found that the peak of Oxygen was strong in the spectrum. Also, the peaks of Ni and Fe were observed in a lesser amount than oxygen which confirmed the composition according to the chemical nature of the material. The molar ratio between Ni:Fe:O is 1:2:8 which has been confirmed from the peaks obtained in the spectrum and the weight content in percentage has been found to be 16:31:53.

The open-aperture z-scan data is found to fit well to a three-photon type absorption (3PA) given by the equation \[ T = \frac{(1 - R_0^2 \exp(-\alpha L))}{\sqrt{\pi} p_0} \int \left[ 1 + p_0 \exp(-2\tau^2) + p_0 \exp(-\tau^2) \right] d\tau \]

Where \( T \) is the net transmission of the samples, \( L \) and \( R \) are the sample length and surface reflectivity respectively, and \( \alpha \) is the linear absorption coefficient. \( p_0 \) in the above equation is given by \[ p_0 = \sqrt{2\gamma(1 - R_0)} I_{0 \text{eff}} \]

where, \( I_0 \) is the on-axis peak intensity, \( L_{\text{eff}} \) is given by \[ \frac{1 - \exp(-2\alpha L)}{2\alpha} \], and \( \gamma \) is the three-photon absorption coefficient.

For the 5ns excitation case (Figure 5) we did z-scans at three different laser pulse energies (100, 200 and 300µJ), and calculated the corresponding \( \gamma \) values, which are shown in figure 6 as a function of the peak input laser intensity. The \( \gamma \) values obtained are in the order of \( 10^{-23} \text{ m}^3/\text{W}^2 \). The increase in the \( \gamma \) value with the input intensity shows that the nonlinear absorption is an effective 3PA process involving excited states in the system. On the other hand with 100 fs excitation the \( \gamma \) value obtained is several orders of magnitude lower (\( 10^{-29} \text{ m}^3/\text{W}^2 \)), and the corresponding z-scan is given in figure 7. This lower value shows that here the nonlinearity arises from a genuine 3PA effect which is a much weaker process compared to the effective 3PA process.

Figure 5: Open aperture Z-Scan curves of NiFe\(_2\)O\(_4\) Nanoparticles for input pulse energies of 100, 200 and 300µJ, for 532nm, 5ns laser pulse excitation. Inset shows the optical limiting curves.

CONCLUSION
Nonlinear optical transmission in Nanocrystalline NiFe\(_2\)O\(_4\) has been investigated using the open aperture Z-Scan technique, in the nanosecond and femtosecond excitation domains. The sample exhibits optical limiting in both cases, but the effective three-photon absorption coefficient obtained for nanosecond excitation is orders of magnitude larger than the genuine three-photon absorption coefficient obtained for femtosecond excitation. The experiments reveal that NiFe\(_2\)O\(_4\) Nanocrystals are optical limiters with a broad temporal response with potential device applications.

REFERENCES
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(Received February 13, 2010; Accepted February 26, 2010)