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Nonlinear optical absorption and optical limiting properties of cadmium ferrite

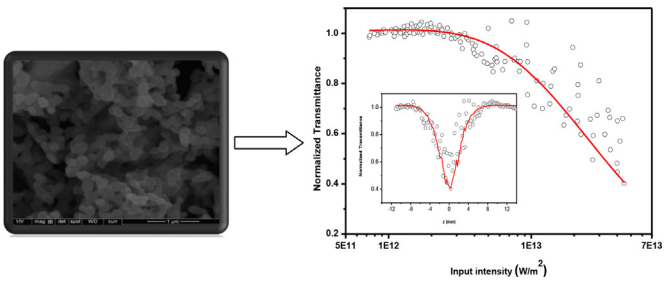
M. Saravanan, T.C. Sabari Girisun*

Nanophotonics Laboratory, School of Physics, Bharathidasan University, Tiruchirappalli, 620 024, India

HIGHLIGHTS

- Spinel cadmium ferrites were synthesized by combustion method.
- As-synthesized sample show prominent hysteresis and heat treated show narrow hysteresis.
- The observed nonlinearity arises due to two photon absorption behavior.
- $CdFe_2O_4$ possesses lower limiting threshold due to the surface spin effect.

GRAPHICAL ABSTRACT



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ABSTRACT

Cadmium ferrite ($CdFe_2O_4$) was synthesized by simple combustion method and characterized by structural (XRD, SEM, EDS, and FTIR), magnetic (VSM) and nonlinear optical (Z-Scan) studies. Powder X-ray diffraction confirms the formation of cubic phase of $CdFe_2O_4$ with the cell constant a = 8.692 Å and a = 8.698 Å for the samples annealed at 500 °C and 800 °C respectively. The average crystallite size was found to increase with an increase in annealing temperature. In the IR spectra of spinel ferrites, the two major absorption bands ν_1 (553.47, 549.61 cm^{-1}) and ν_2 (410.75, 424.26 cm^{-1}) corresponds to the vibration of tetrahedral and octahedral sites of $CdFe_2O_4$. VSM studies shows that material is antiferromagnetic in nature, when heated at higher temperature. Optical nonlinearity of the samples was studied by open aperture Z-scan technique using Q-switched Nd:YAG (532 nm, 5 ns, 10 Hz) laser. The material possesses reverse saturable absorption and can be ascribed due to two photon absorption process. Also the materials exhibit optical limiting behavior with onset limiting value of 4.45 × 10^{12} W/m^2, 3.59 × 10^{12} W/m^2 for the samples annealed at 500 °C and 800 °C respectively.

1. Introduction

The pulsed lasers are used for countless applications and are wide spread in the realms of industry, communications and warfare. With a substantial increase in the risk of handling intense laser pulses, optical limiting has become an important phenomenon of photonics. Optical limiters are devices that show an induced net decrease in transmittance at higher light fluences. These are very useful for protecting sensitive devices and eyes from laser induced damage. With nanosecond pulse excitation, optical limiting property could be achieved by accumulative nonlinear optical (NLO) phenomena like excited state absorption, two/three photon absorption, and free carrier absorption [1]. Over the years, ferrite materials such as normal, inverse and mixed spinel have been studied for their optical limiting performances. Especially nanosized spinel ferries have shown exceptional

* Corresponding author.
E-mail address: sabarigirisun@bdu.ac.in (T.C.S. Girisun).

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optical and magnetic properties demonstrating potential optical limiting applications [2–4]. In general spinel ferrites are represented with chemical formula AB_2O_4, where A and B represents divalent and trivalent cations which include Mg, Cd, Zn, Fe and Mn.

The optical properties of the magnetic spinel ferrites depend on the magnetic interaction and distribution of cation in the sub lattices. The nonlinear response of these magnetic materials can be tailored by the application of an external magnetic field which is of great interest to the technological world. Such a system requires an interaction between the magnetic susceptibility and nonlinear absorption of the material. Cadmium ferrites nanoparticles are one such normal spinel ferrite system which has nonmagnetic (Cd^{2+}) material coordinate with magnetic (Fe^{3+}) material occupying the tetrahedral (A) and octahedral (B) sites [5]. Among the various methods available for synthesis of cubic ferrite, the combustion reaction [6,7] and coprecipitation [8] stands out as an alternative and highly promising method. In particular, combustion method is simple, fast and inexpensive since it does not involve intermediate decomposition steps. Also it is easy to control the stoichiometry and crystallite size which have important influence on the magnetic and optical properties of the ferrite. The present work describes the preparation of $CdFe_2O_4$ by simple combustion method using glycine as fuel material. The obtained powders were annealed at two different temperature and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), vibrating sample magnetometer (VSM) and Z-scan technique (open aperture). By tuning the magnetic property of the material, the magnetic anisotropy of the ion at the interfaces can be reduced [9] which can result in strong nonlinear optical response. Hence the magnetic and nonlinear optical properties of the heat treated materials were analyzed in detail. To the best of our knowledge, optical limiting behavior of cadmium ferrite and the possible mechanism is reported for the first time in literature.

2. Experiment

2.1. Material preparation

The thermochemical concepts used in propellant chemistry and explosives are the fundamentals of the combustion technique. This method exploits a rapid exothermic and self sustaining chemical reaction between the metal salts and a suitable organic fuel. As stated in the propellant chemistry, the elements H, C, Cd and Fe are considered as reducing elements, element oxygen is considered as an oxidizing element, and the valency of element nitrogen is considered to be zero [10]. In the present work, cadmium ferrite samples were synthesized by combustion reaction method using Cadmium nitrate [$Cd(NO_3)_2.4H_2O$], Ferric nitrate [$Fe(NO_3)_3.9H_2O$] and Glycine [H_2NCH_2COOH] as starting materials. Based on the thermochemical concepts of propellant chemistry, the molar ratio of nitrates to glycine was taken as 3:5. It is the ratio of valencies of nitrates to fuel, which provides the maximum exothermicity during the reaction. The solution was kept under continuous stirring for half an hour and simultaneously heated on a magnetic hot plate. After the removal of water content, the solution turns to gel form. Persisted heating provides a spinel phase $CdFe_2O_4$ powder through a single step combustion reaction with evolution of voluminous gas. The obtained powders were annealed at 500 °C (sample (a)) and 800 °C (sample (b)) for one hour using muffle furnace and the final spinel ferrite powder formed was collected for subsequent investigations.

2.2. Characterization

The crystalline spinel phase present in the materials annealed at various temperature were identified by powder X-ray diffraction using CuKα radiation employing a scanning rate of 0.02 s^{-1} in the angle of 10–80°. The lattice parameters of the samples were estimated using the relation, $a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$ [11]. Also the X-ray densities (d_x) of the samples were calculated from the lattice constant using the relations, $d_x = ZM/Na^3$ where Z is number of molecules per unit cell of spinel lattice, *M* is molecular weight of the sample, *N* is the Avogadro's number and *a* is the lattice constant of the sample [12]. The crystallite size of the material was determined from X-ray line broadening method using the Scherrer equation, $D = K\lambda/\beta \cos\theta$ where, *D* is the crystallite size, λ is the wavelength of X-ray beam, *K* is the constant (0.94), β is the peak width at half maximum intensity and θ is the peak position. IR studies were carried out with JASCO 460 PLUS FTIR spectrometer from 400 to 4000 cm^{-1} to identify the various functional groups of the ferrites. Morphologies of the samples were investigated by scanning electron microscope (SEM) analysis using Hitachi SEM400. The chemical compositions were analyzed through energy dispersive spectroscopy (EDS). Magnetic hysteresis study of thermally treated ferrites were carried out using vibrating sample magnetometer (VSM; Lake Shore: model: 7404) in the magnetic field range of −1.5 T to +1.5 T. The values of remanence magnetization (M_r) and saturation magnetization (M_s) were also estimated from the recorded hysteresis plot. The experimental magnetic moment was calculated using the formulas, $\mu_B = M_w \times M_s/5585$ where, M_w is the molecular weight of the sample and M_s is the saturation magnetization [13].

The nonlinear optical response was studied by open aperture Z-scan technique using a Q-switched Nd:YAG (532 nm, 5 ns, 100 μJ) laser. Firstly, the prepared powder samples were dispersed by ultrasonication in ethylene glycol. The dispersed solution is kept in a focused beam of laser in a Z-direction for excitation. Automated Z-scan setup uses a precision stepper motor to control the translation stage to move the samples along the positive and negative Z direction. The input and transmitted energy of the samples were measured using two pyroelectric energy probes (Rjp 735, Laser probe Inc). Transmission data recorded at each Z position is plotted as patterns (Z-scan curve).

3. Results and discussion

3.1. Structural characterization

The recorded XRD pattern is as shown in Fig. 1 which indicates the formation of cadmium ferrite. All the main peaks were indexed and it coincides very well with literature data (JCPDS: 79-1155). The major peak located at 34° corresponds to the (311) plane which can be readily ascribed to the characteristic peaks of the cubic phase of $CdFe_2O_4$ (spinel ferrites). The estimated cell constant a = 8.692 Å and a = 8.698 Å for samples (a) and (b) agrees with the reference value a = 8.708 Å (JCPDS: 79-1155). The sharp and narrow peaks in the sample (b) indicate the increase in the crystallinity and crystallite size of the sample. The presence of traces of α-Fe_2O_3 hematite impurity in the samples was identified and is shown in the XRD pattern. However at elevated annealing temperature, the secondary phases get suppressed, which is evident from the decrease in the intensity of minor peaks. Generally the X-ray density reflects on the packing of the atom in a unit cell and it is calculated to be 5.82 and 5.81 g/cm^3 for sample (a) and (b) respectively. The obtained values are consistent with the X-ray density values of $CdFe_2O_4$ nanoparticles prepared by ceramic method [14]. By Scherrer formula, the average crystallite size is calculated to be 35 nm and 78 nm for sample (a) and (b) respectively.

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