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Nonlinear optical properties of nematic liquid crystal doped with different compositional percentage of synthesis of Fe_3O_4 nanoparticles

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ABSTRACT

In this research, Fe_3O_4 nanoparticles were synthesized and analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The synthesized Fe_3O_4 with different compositional percentage doped in an E7 nematic liquid crystal (NLC). Nonlinearity of pure and doped NLC with Fe_3O_4 nanoparticles were studied by z-scan technique (close aperture and open aperture z-scan). The experimental results show that the nonlinear optical responses of Fe_3O_4 nanoparticles doped E7 can be changed by varying the compositional percentage of Fe_3O_4 nanoparticles. A small compositional percentage of Fe_3O_4 nanoparticles, 1% W/W, dispersing in a NLC showed improved nonlinearity.

1. Introduction

The advanced research in nonlinear optics depend on the development of new materials with strong nonlinear optical effects [1]. Recently, using of nanomaterials is one of the most fruitful factors in new approaches to the nonlinear optics field. Additionally, liquid crystals are very welcoming to other materials which are mixed to nanoparticles or imbedded into other materials/confinements very well. This creates an opportunity for the construction of a whole new world of composite materials such as liquid crystalline nanomaterials [2]. It has been disclosed that many properties of liquid crystal can be improved and enhanced by doping with ferromagnetic grains, which are favorable for practical applications [3]. Among the various mesophases of liquid crystals, nematic liquid crystals (NLCs) exhibit a high optical anisotropy and large nonlinearities [4,5]. The practical operating temperatures in eutectic mixture liquid crystals offer a wide range for applications in displaying devices, privacy windows, optical shutters, light valve, light control applications, etc. [6].

Iron ferrite, Fe_3O_4, is a traditional magnetic material that has been used in magnetic storage media, solar energy transformation, electronics, ferrofluids, catalysis [7,8] separation cells, tumor hyperthermia [9], audio voice coil-damping, inertia-damping apparatuses, bearings, stepping motors and vacuum seals [10]. Several different synthetic routes have been developed for preparing the wide range of ferromagnetic spheroidal particles, and controlling their shapes [11]. Co-precipitation is a facile and convenient method for synthesizing iron oxides (either Fe_3O_4 or g-Fe_2O_3) from aqueous Fe^{2+}/Fe^{3+} salt solutions by adding a base under inert atmosphere at room temperature or elevated temperature [12].

In this work, we reported the synthesis of Fe_3O_4 nanoparticles (nps) via chemical co-precipitation method and analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Furthermore, the influence of compositional percentage of these nps has been shown in the nonlinear optical properties of NLC using the z-scan technique.

2. Materials and methods

2.1. Sample preparation

The ferronematic materials investigated in this work are a mixture of Fe_3O_4 nps and nematic liquid crystals. Fe_3O_4 nps with typical sizes of 34 nm was synthesized by co-precipitation method and used as the guest. The nematic LC mixture E7 produced by the liquid crystal laboratory at the Warsaw University of Technology was used as a host. The different compositional percentages of Fe_3O_4 nps in guest–host system were 0% W/W, 1% W/W, 5% W/W and 10% W/W. The guest–host cells consisted of two glass plates with an inner area of 1 cm × 2 cm and thickness of 1 mm. Before construction of the cells, the glass substrates were dip coated with lecithin for homeotropical alignment. Measurement cell was made up of two glass slides separated by Mylar sheets having 28 μm thickness. The studied ferronematic samples obtained with doped nps in E7 mixture via mechanical shaking using an ultrasonicator (36 kHz). Both undoped and Fe_3O_4 nps doped NLC samples were filled into empty cells at a higher temperature than the isotropic temperature of the NLC via capillary action technique [13–16]. They were used to determine the nonlinear responses of Fe_3O_4 nps in NLC mixtures.

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2.2. Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nps were synthesized by using chemical co-precipitation, in which Iron (II) and (III) chloride salts were added to ammonium hydroxide [9,17]. Then their magnetic property was confirmed by observing their response to a magnet. The chemical reaction can be expressed as:

$$2FeCl_3.6H_2O + FeCl_2.4H_2O + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 20H_2O \quad (1)$$

The NH_4Cl is separated from the precipitant of this reaction by washing and centrifuging it several times with de-ionized water and then Fe_3O_4 remains. Finally, we coated the nps with oleic acid as a surfactant in order to prevent them from agglomerating.

2.3. Z-scan technique

2.3.1. Z-scan theory

The z-scan technique is a very popular and sensitive single beam method for measuring the nonlinearity of optical materials. The z-scan method involves two experimental set-ups: 1 — with a small aperture (closed aperture) and 2 — without any aperture (open aperture), in order to resolve the nonlinear refraction index, n_2 and absorption coefficient, β [18]. In closed aperture (CA) z-scan measurement, an aperture is placed to prevent some of the light from reaching the detector. When it was open aperture (OA) measurement, aperture was replaced by a lens to collect all the light into power meter's detector ($S = 1$, the total transmittance) [19].

The nonlinear refractive index, n_2 in the expression $n(I) = n_0 + n_2 I$, was calculated as follows: where n_0 is the linear refractive index and I is the intensity of the incident laser light [18]. For the closed-aperture condition the normalized transmission is given by,

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\Phi_0| \text{where} |\Delta\Phi_0| \leq \pi. \quad (2)$$

In which ΔT_{p-v} is the difference between the normalized peak transmittance and valley transmittance and S is the aperture's linear transmittance. $|\Delta\Phi_0|$ and n_2 have a relationship through the following expression.

$$|\Delta\Phi_0| = (2\pi/\lambda) n_2 I_0 L_{eff} \quad (3)$$

Where $L_{eff} = (1 - e^{-\alpha L})/\alpha$ is the effective thickness of the sample, α is the linear (low intensity) absorption coefficient, L is the thickness of samples, $I_0 = 2P_{in}/\pi\omega_0^2$ is the incident intensity at focal point, P_{in} is the laser power, ω_0 is the beam radius at the focal point and λ is the wavelength of laser light. The nonlinear behavior of the sample is equivalent to the formation of an induced positive or negative lens as self-focusing (positive) or self-defocusing (negative) [20–23].

The nonlinear absorption coefficient, β in the expression $\alpha(I) = \alpha + \beta I$, was obtained from open aperture z-scan [18]. The normalized transmittance under open-aperture conditions is given by

$$T_{norm}(z) = Ln(1 + q_0(z,t))/q_0(z,t) \quad (4)$$

Where $q_0(z,t) = \beta I_0 L_{eff}/(1 + z^2/z_0^2)$, $z_0 = k\omega_0^2/2$ is the diffraction length of the beam, z is the distance from the focal point and $k = 2\pi/\lambda$ is the wave vector [18,24].

2.3.2. Z-scan set up

The experimental setup of used z-scan technique is shown schematically in Fig. 1 [25]. The z-scan technique was implemented using a linear polarized Gaussian continuous wave (CW) Nd:Yag laser at $\lambda = 532$ nm with a power of 100 mW as the light source. The power of the laser was reduced to 10 mW by adequate filters. It is important to choose a low intensity for laser to avoid the thermal effects [26].

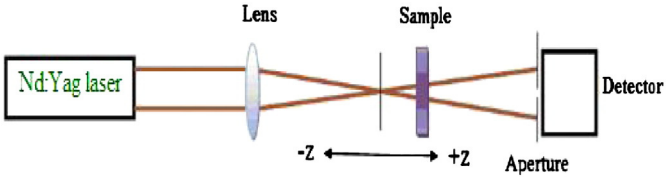

Fig. 1. Schematic diagram of the experimental arrangement for close aperture z-scan setup.

The wavelength of laser is close to maximum absorption peak of Fe_3O_4 nps in NLC ($\lambda_{max} = 450$ nm).

3. Results and discussion

3.1. Characterization of Fe_3O_4 nanoparticles

The synthesized Fe_3O_4 nps were characterized by means of XRD and SEM studies. The X-ray diffraction (XRD) (Model: Philips, X'pert) with Ni-filter Cu K_α radiation is used to identify crystalline structure and crystallite size of the samples. Fig. 2 shows the XRD pattern of Fe_3O_4 nps. The crystallite size of the Fe_3O_4 nps, D, was calculated by using the Debye–Scherre (Eq. (5)) from the major diffraction peak of the corresponding Fe_3O_4

$$D = K\lambda/\beta\cos\theta \quad (5)$$

where K is a constant (0.9), λ is the X-ray wavelength used (0.15406 nm), θ is half the scattering angle (the Bragg diffraction angle), and β is the full-width at half-maximum (FWHM) of the X-ray diffraction line (additional peak broadening) in radians[27–29].

Table 1 presents the XRD spectral data for the Fe_3O_4 nps. From the above equation, the average crystallite size was found to be 20.7 nm. The crystal planes correspond to a cubic lattice structure of Fe_3O_4 nps (Reference code: 03-065-3107). For cubic crystals, the lattice constant, α can be found from below relation:

$$\alpha = d\sqrt{h^2 + k^2 + l^2} \quad (6)$$

where d is the spacing between adjacent (hkl) lattice planes and h, k, l are miller indices. The average lattice constant was calculated to be about 0.837 nm.

Scanning electron microscopy (SEM) was performed using a Hitachi S-4160 SEM to investigate the morphology and particle size of Fe_3O_4 nps [27,29]. SEM image of Fe_3O_4 nps is shown in Fig. 3. SEM photograph

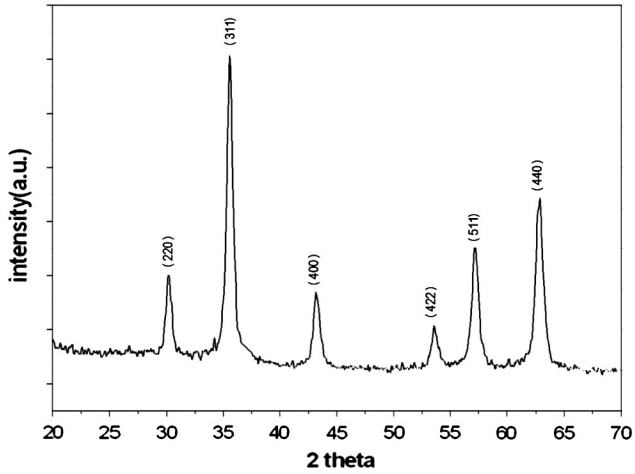

Fig. 2. XRD pattern of synthesized Fe_3O_4 nanoparticles matching to the standard JCPDS no. [03-065-3107].