

Nonlinear Optical Characterization of the Ag Nanoparticles Doped in Polyvinyl Alcohol Films¹

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Abstract—The effect of silver nanoparticles doped in polyvinyl alcohol (PVA) on the nonlinear optical properties of composite films is studied experimentally. Samples are PVA films of 0.14 mm thickness doped with different concentrations of silver nanoparticles. Nonlinear optical properties of doped polymer films are studied experimentally employing *Z*-scan techniques. Experiments are performed using the second harmonic of a continuous Nd–Yag laser beam at 532 nm wavelength and 45 mW power. The effect of nonlinear refractive index of samples is obtained by measuring the profile of propagated beam through the samples and their nonlinear refractive index is found to be negative. The nonlinear absorption coefficient is calculated using open aperture *Z*-scan data while its nonlinear refractive index is measured using the closed aperture *Z*-scan data, leads to measuring the third order susceptibility $|\chi^{(3)}|$. Real and imaginary parts of the third-order nonlinear optical susceptibility $|\chi^{(3)}|$ are decrease with increasing the concentration of Ag nanoparticles in the films. The values of thermo-optic coefficient are determined at different concentrations of silver nanoparticles for samples.

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1. INTRODUCTION

Noble metal nanoparticles exhibit wide range of applications in different fields of science and engineering such as catalysts, bactericides and optical materials [1–4]. Recently, there has been growing interest in the nonlinear optical properties of metal nanocomposite films, particularly of metal nanoparticles doped in polymer films [5, 6]. Material with large third order nonlinear susceptibilities and nonlinear optical response are attractive for many applications such as electronic and optical devices, chemical and biological sensors, optical energy transport, and thermal therapy [7–12].

The nonlinear properties of metal nanoparticles can be modulated by variation of their concentration, size and shape. Metal nanoparticles are usually dispersed in host matrices such as polymers, colloidal solutions, LB films, glasses and zeolites [13]. When the nanoparticles of noble metals are embedded in dielectric matrices, the films will exhibit specific optical absorption and large third order optical nonlinearity, which have potential application in nonlinear optical devices and optical limiters. Furthermore, it is proven that nonlinear optical properties of dielectric matrices can enhance by mixing with metal nanoparticles.

The *Z*-scan technique was developed to measure the magnitude and sign of nonlinear refraction

(NLR), by the Mansoor Sheik-Bahae et al. (1998). It is also useful for characterizing nonlinear absorption (NLA). The *Z*-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for separately determining the nonlinear changes in index refraction and changes in absorption. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the interpretation. In most experiments the index change, Δn , and absorption change, $\Delta\alpha$, can be determined directly from the data without resorting to computer fitting. However, it must always be recognized that this method is sensitive to all nonlinear optical mechanisms that give rise to a change of the refractive index and/or absorption coefficient, so that determining the underlying physical processes present from a *Z*-scan is not in general possible [14]. This method utilizes a tightly focused laser beam that is intense enough to access nonlinearities in a sample. The sample with thickness smaller than the diffraction length of the focused beam (a thin medium) passes through the focal point of the beam and we measure the transmittance of a nonlinear medium as a function of the sample position *z* measured with respect to the focal plane (Fig. 1). These changes in its transmittance due to NLA and NLR are measured by an open aperture and closed aperture, respectively. For NLR we measure the transmittance of a nonlinear medium through a finite aperture in the far field as a function of the sam-

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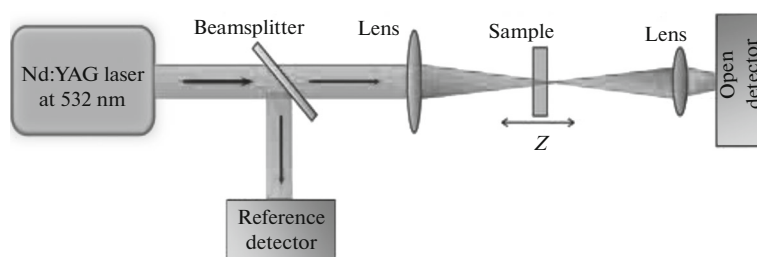


Fig. 1. Schematic diagram of experimental open Z-scan setup.

ple position z measured with respect to the focal plane. The converging and diverging of the beam (allowing more and less of the beam to pass through the aperture, respectively) made changes in the refractive index. In fact, nonlinear refractive index of the sample when its thickness is smaller than the diffraction length of the focused beam, makes it to act as a thin lens with variable focal length. A prefocal valley and postfocal peak is observed for a positive change in refraction and a preffocal peak and a post-focal valley is observed for a negative change in refraction. In the open aperture technique after the beam is passed through the sample it is focused directly into a detector. As the sample travels through the focus of the initial beam, the transmittance either increases or decreases (depending on the nonlinearity of the sample) and the detector receives more or less light than the linear transmittance, yielding a hump or dip in the curve of transmittance as a function of sample position [7, 14].

In this work, we presented our studies of nonlinear optical properties of silver nanoparticles with various concentration which were prepared by laser ablation, doped in PVA polymer. The optical nonlinearity of the polymer films doped with silver nanoparticles is measured by Z-scan technique. The nonlinear refractive index and nonlinear absorption coefficient are investigated using a continuous wave laser beam with wavelength $\lambda = 532$ nm. Z-scan measurements are carried out in three different concentrations of the same thickness of samples. The negative refractive index and two photon absorption coefficient are measured for these films. The third order nonlinear refractive index and absorption coefficient are found to be dependent on the concentration within the range of study. It is well known that concentration of Ag nanoparticles dependence plays a very important role in the nonlinear optical action.

This manuscript is organized as follows: following the introduction in Sec. 1, experimental details are presented in Sec. 2, Sec. 3 is devoted to results and discussion and Sec. 4 includes conclusion.

2. EXPERIMENTAL DETAILS

Nanoparticles (NPs) were prepared by ablation of a high purity silver bulk in distilled water, using the fun-

damental harmonic of a Nd:YAG laser operating at 1064 nm with pulse width of 7 ns and 10 Hz repetition rate. Silver bulk was placed at the bottom of a water contain with its surface at the focal point of an 80 mm convex lens. Height of water on the silver target was 12 mm. Laser beam diameter was 2 mm before the lens and has been calculated to be 30 μm on the surface of the target. The volume of the water in the ablation contain was 20 mL and silver target was ablated with 500 laser pulses at different energies. Samples 1–3 (S1 to S3) were prepared with laser pulse fluencies of 1.5, 2, 3 J/cm^2 , respectively.

By weighting the dried target before and after ablation process the mass of ablated Ag nanoparticles were measured to be 3.7×10^{-4} , 4×10^{-4} , 6.5×10^{-4} g for S1, S2, and S3, respectively. PVA films were prepared by dissolving 1 g of PVA powder in 20 mL distilled water at 57°C . Mixture was stirred for two hours continuously to form a viscous solution. The PVA powder was provided by Merck Co. (Germany). After complete desolation, 8 mL of silver nanoparticles suspension was added to the 20 mL aqueous PVA solution and finally samples was left to dry on a plane surface for 24 h at room temperature in close atmosphere to produce 3 samples of 0.14 mm thickness uniform silver nanoparticles doped PVA films. S1 to S3 are PVA films which are doped with sample 1 to 3 nanoparticles.

TEM micrographs were taken using CM120 system form PHILIPS Co. The transmission spectrum of samples was recorded on a UV-Vis-NIR spectrophotometer from Varian Cary-500 Scan. After characterizing the nanoparticles solution, Z-scan experiments were carried out to study the nonlinear optical properties of samples as a function of concentration. Indeed, the optical properties of Ag nanoparticles doped PVA films were studied by means of transmittance and Z-scan measurements using a 45 mW continuous wave laser operate at 532 nm wavelength with single mode TEM₀₀ Gaussian beam. The M² factor of beam was 1.2. The beam was focused onto the sample by using a 6.5 mm focal length lens. The spot size of the beam was 0.25 cm before the lens, and Rayleigh length was 3.68 mm. The film was moved in the z direction by using a translation system along the propagation direction through the focusing area. The transmitted

The value of n_2 , β , $\chi^{(3)}$ and dn/dT of doped polymer films

Sample	$n_2 \times 10^{-7}$, cm ² /W	$\beta \times 10^{-3}$, cm/W	$\text{Re}(\chi^{(3)}) \times 10^{-6}$, esu	$\text{Im}(\chi^{(3)}) \times 10^{-7}$, esu	$\chi^{(3)} \times 10^{-6}$, esu	$dn/dT \times 10^{-5}$, K ⁻¹
S1	-6.01	2.15	-4.72	7.16	4.77	5.34
S2	-6.76	2.29	-4.47	6.41	4.51	6.67
S3	-8.82	2.93	-4.09	5.76	4.13	8.97

power was measured by a Gentec-Eo laser power meter.

3. RESULTS AND DISCUSSION

TEM images of nanoparticles are presented in Figs. 2a–2c. In this set of images, the interbrain structure can be observed. Produced nanoparticles are spherical without any aggregation. The average size distribution of nanoparticles for all three samples can be observed in Fig. 2d. These graphs are plotted using the “measurement” software. It can be seen that the average size for these nanoparticles was estimated to be 11 nm.

The variation of transmittance (T) as a function of wavelength for samples 1 to 3 was recorded at room temperature and is shown in Fig. 3. Pure PVA is a col-

orless polymer without any noticeable absorption in the visible range. The sharp increase observed in transmittance spectrum in the range of 210 to 248 nm is due to the presence of the PVA polymer bandgap [15]. This is clearly indicated that with adding nano-Ag in PVA polymer, a valley at 421 nm has been created, that its intensity continuously increasing with increasing concentration of the dopant. This valley is attributed to the formation of charge transfer complexes [16]. The appearance of this valley in the visible region is due to the surface plasmon resonance (SPR) nature of the Ag nanoparticles embedded in PVA polymer dielectric medium.

The Z-scan technique measures the change in intensity of a focused beam as a sample travels axially (the z -axis) through the beam waist with $z = 0$ at the focal plane. There are two variations of Z-scan, each of which yields a different component of $\chi^{(3)}$. The closed aperture setup gives the real component corresponding to nonlinear refraction; and the open aperture, the imaginary component corresponding to nonlinear absorption.

Figure 4 shows the normalized transmittance of closed aperture Z-scan as a function of distance from the focus point of the Gaussian beam ($z = 0$). The peak followed by a valley in the transmittance is obtained from the closed aperture Z-scan data, indicates that the sign of the refraction index nonlinearity

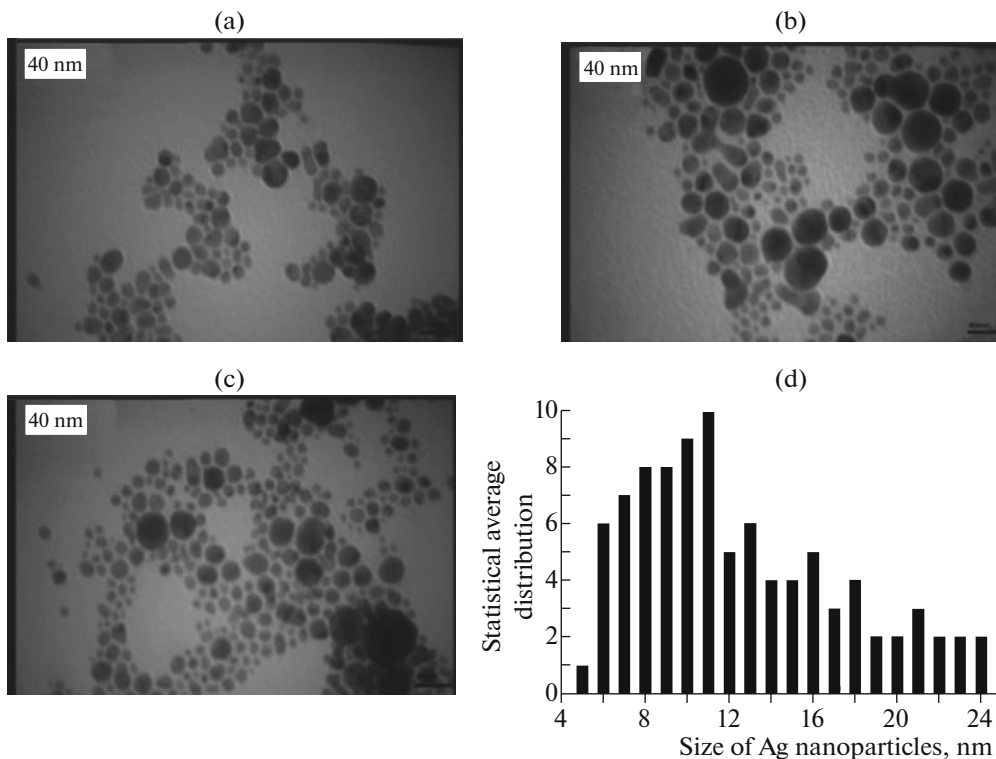


Fig. 2. TEM images: (a) S1 (1.5 J/cm²), (b) S2 (2 J/cm²), (c) S3 (3 J/cm²); (d) average size distribution of Ag nanoparticle generated in distilled water with laser ablation method.

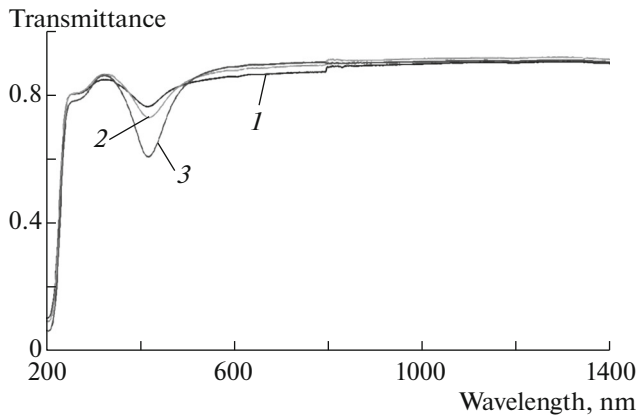


Fig. 3. Optical transmittance spectrum of samples: S1 (1), S2 (2), S3 (3).

is negative, i.e., self-defocusing. The self-defocusing effect is due to the reorientation Kerr effect (the magneto-optical Kerr effect) [17]. In particular, we observe that with increase of the silver nanoparticles concentration in the PVA polymer films the shape of the closed aperture one remains unchanged. However, the whole doped samples have a nonlinear refractive index properties, the normalized transmission curve of closed aperture data does not show a perfect symmetry curve. According to a pair of simple equations: $d(\Delta\phi)/dz = \Delta n(I)k$ and $dI/dz = -\alpha(I)I$, that k is wave vector, in the propagation depth in the samples for Gaussian beam, the nonlinear refraction is related to the on-axis phase shift $\delta\phi$ at the focus and $\alpha(I)$ includes linear and nonlinear absorption terms [18]. When the data of normalized transmittance in closed aperture Z -scan show a perfect symmetry curves the absorption coefficient is very small so the open aperture Z -scan curves for the hypothetical sample are linear (not shown). Indeed in Fig. 3, the valley and the peak of the closed aperture Z -scan is asymmetric due to both the axial phase shift $\Delta\phi_0$ and the nonlinear absorption [18–21]. The nonlinear refractive index can be calculated from the normalized transmittance data of closed aperture measurement which can be written as follows [18]:

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25} \Delta\phi_0, \quad (\Delta\phi_0 \leq \pi), \quad (1)$$

where $\Delta T_{p-v} = T_p - T_v$ is the difference between normalized peak and valley transmittance, $S = 1 - \exp(-2r_a^2/w_a^2)$ is the aperture linear transmittance with r_a denoting the radius aperture and w_a denoting beam radius at the aperture in the linear region and $\Delta\phi_0$ is the induced phase distortion of radiation passed through the sample. The nonlinear refractive index n_2 can be finally calculated by the following equation [18]:

$$n_2 = \lambda \Delta\phi_0 / 2\pi I_0 L_{ef}, \quad (2)$$

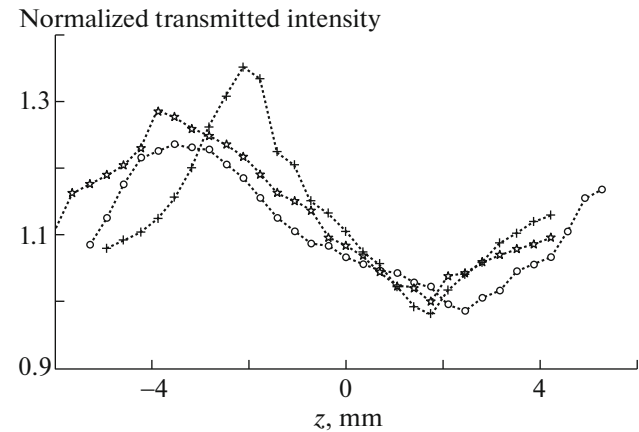


Fig. 4. Closed aperture Z -scan data for doped samples: S1 (circles), S2 (asterisks), S3 (crosses).

where $L_{ef} = (1 - \exp(-\alpha L))/\alpha$ is known as the effective thickness of the sample, L is the thickness of the films, λ is the laser wavelength and $I_0 = 8 \times 10^3 \text{ kW/m}^2$ is the Gaussian beam intensity at the focal plane and α is the linear absorption coefficient at $\lambda = 532 \text{ nm}$. This linear absorption of the doped samples decreased due to the increasing of the transmittance from 84.2% in S1 to 85.6% in S2 and 86.1% in S3, with increasing concentration of silver nanoparticles. The calculated values of the nonlinear refractive index for the samples 1 to 3 are listed in table. We observed that the nonlinear refractive index tends to increase with increasing the concentration of the Ag nanoparticles in the structure of films. The rate of increasing in nonlinear refractive index is not same for all doped samples. This is because of the increasing concentration of silver nanoparticles which leads to increasing the numbers of metal nanoparticles in effective thickness, so the interaction of nanoparticles which are located in the beam path with laser beam will enhance. By increasing these interactions, the nonlinear refractive index is increased.

The variation of ΔT_{p-v} is a function of $\Delta\phi_0$ for a specific aperture size. In this case ΔT_{p-v} with increasing concentration of silver nanoparticles in films are increased. In fact, the linear behavior of ΔT_{p-v} with increasing concentration of Ag nanoparticles follows Eq. (1) as derived for a cubic nonlinearity [18]. Also Δz_{p-v} showed a decrease with increasing concentration of Ag nanoparticles in PVA matrix so the beam divergence declined.

Figure 5 shows the results of open aperture Z -scan experiments. As it is seen, the transmission at the focus decreases with increasing sample concentration. The valley in the open aperture Z -scan experiment indicates that the sign of nonlinear absorption coefficient of samples is positive. One obtains that higher concentration of the sample gives better nonlinear optical properties. For semiconductors that have two

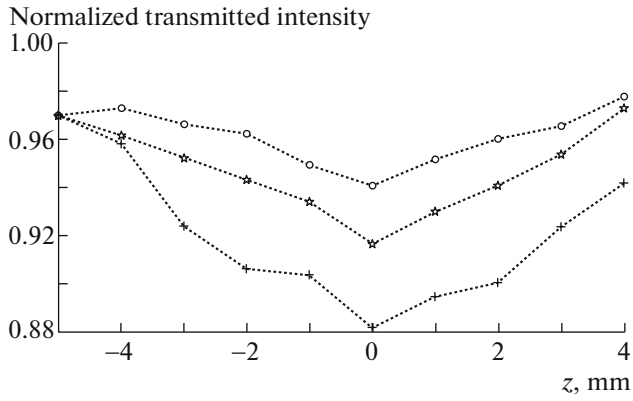


Fig. 5. Open aperture Z-scan data for doped samples: S1 (circles), S2 (asterisks), S3 (crosses).

conditions, positive nonlinear absorption coefficient and $E_g < 2\omega\hbar < 2E_g$, where E_g is the bandgap energy and ω is optical frequency, we analyze two-photon absorption (2PA) [18]. Here, the samples with average bandgap energy of $E_g = 4.5$ eV are a two-photon absorber at this wavelength, therefore they show optical limiting behavior. Since the laser beam was single TEM₀₀ Gaussian beam, we can use the following equation to calculate the normalized transmittance for the open aperture condition:

$$T(z, s = 1) = \sum_{m=0}^{\infty} [-q_0(z)]^m / (m+1)^{3/2}. \quad (3)$$

For $q_0 < 1$, where

$$q_0(z) = I_0 L_{\text{eff}} \beta / (1 + z^2/z_0^2), \quad (4)$$

where $z_0 = k\omega_0^2/2$ is the diffraction length of the focused beam. Similar to closed aperture experiments, the laser beam intensity of $I_0 = 8 \times 10^3$ kW/m² is used in this part. The calculated values of β are presented in table. Numerical values are indicative of increased two-photon absorption at the focus with increasing concentration of the Ag nanoparticles of samples. Thus it could be a good candidate for nonlinear optical devices.

In electromagnetism, the electric susceptibility is a dimensionless proportionality constant that indicates the degree of polarization of a dielectric material in response to an applied electric field. The greater the electric susceptibility, the greater the ability of a material to polarize in response to the field, and thereby reduce the total electric field inside the material. In many materials the polarizability starts to saturate at high values of electric field. This saturation can be modeled by a nonlinear susceptibility [22]. These susceptibilities are important in nonlinear optics and lead to effects such as self-defocusing effect in present samples. The real and imaginary parts of $\chi^{(3)}$ describe NLR

and NLA or gain. This can be understood by considering situations in which the nonlinear polarization is at one of the driving frequencies [17]. The real and imaginary parts of the third order nonlinear optical susceptibility $\chi^{(3)}$ can be the following equations:

$$\text{Re} \chi^{(3)} (\text{esu}) = (10^{-4} \epsilon_0 c^2 n_0^2 / \pi) n_2, \text{ in } (\text{cm}^2/\text{W}), \quad (5)$$

and

$$\text{Im} \chi^{(3)} (\text{esu}) = (10^{-2} \epsilon_0 c^2 n_0^2 \lambda / 4\pi^2) \beta, \text{ in } (\text{cm}/\text{W}), \quad (6)$$

where ϵ_0 is the vacuum permittivity, c is the speed of light in the vacuum and n_0 is the linear refractive index. Based on this theory, results of experiments are used to calculate $\text{Re} \chi^{(3)}$ and $\text{Im} \chi^{(3)}$ which are presented in table. The values of $\text{Re} \chi^{(3)}$ and $\text{Im} \chi^{(3)}$ decrease with increasing the concentration of Ag nanoparticles in PVA, films because the linear refractive index of the dielectric medium has been declined after adding Ag nanoparticles in PVA polymer and it decreases with increasing concentration of Ag nanoparticles in PVA matrix. This property is inherent in all conductors and due to localized fluctuation of charged particles in medium [23]. Thus the absolute value of the third order nonlinear optical susceptibility was calculated as

$$|\chi^{(3)}| = \{[\text{Re}(\chi^{(3)})]^2 + [\text{Im}(\chi^{(3)})]^2\}^{1/2}. \quad (7)$$

The values of the third order nonlinear susceptibility obtained for the present samples are completely listed in table.

Thermal processes can lead to large nonlinear optical effects. The thermally induced nonlinearity denotes temporal variation of optical parameters (in particular, refractive index) due to linear and/or nonlinear absorption in medium followed by a nonradiative relaxation down to the ground state. The laser heating leads to the generation of acoustic wave that changes the medium density followed by a variation of refractive index [24, 25]. This process is slow and can be observed in the case of CW laser, long-pulse laser. The origin of thermal nonlinear optical effects is that some fraction of the incident laser power is absorbed in passing through an optical material. The temperature of the illuminated portion of the material consequently increases, which leads to a change in the refractive index of the material [26–28]. Thermal effects can be described mathematically by assuming that the refractive index varies with temperature [25] according to

$$\Delta n = (dn/dT) \Delta T, \quad (8)$$

where $n = n_2 I_0$ is the maximum change in the refractive index of material due to thermal effects and dn/dT is the thermo-optic coefficient. In Eq. (8), T is defined as

$$\Delta T = \alpha I_0 \omega_0^2 / 4k. \quad (9)$$

In this equation, $k = 0.17$ W m⁻¹ K⁻¹ is thermal conductivity of PVA polymer and ω_0 is the waist width at focus. Magnitudes of temperature dependence of

the nonlinear refractive index and the variation of nonlinear refractive index are presented in table. Because of the temperature elevation in the focal spot, the thermal convection effects of warm doped samples give the main effect in heating induced nonlinearity for CW excitation. As result, a nonlocal interaction between the radiation light and the sample must be considered for analyzing the closed Z -scan measurement result. This method for calculation of nonlinear refractive index and thermal effect is called the thermal thin lens model. The defocusing effect shown in closed Z -scan curve can be attributed to a thermal nonlinearity resulting from absorption of radiation at 532 nm. Localized absorption of a tightly focused beam propagating through an absorbing sample medium produces a spatial distribution of temperature in the dielectric medium and consequently a spatial variation of the refractive index that acts as a thermal lens resulting in phase distortion of the propagating beam so we saw that with increasing concentration of silver nanoparticles the beam divergence declined. In other words, increasing the concentration of silver nanoparticles in pure PVA polymer film leads to increase of die thermal effects in the doped films.

CONCLUSIONS

Preparation of silver nanoparticles by laser ablation method at different fluencies of laser pulse in pure water is investigated. The results of transmittance showed plasmonic absorption peak of silver nanoparticles. In closed Z -scan experiment found that the laser beam is defocused after propagating through the nanoparticle solution we confirm that the nonlinear refractive index of samples are negative. The nonlinear refractive index, n_2 , and the nonlinear absorption coefficient, β , of samples is increased by increasing concentration of Ag nanoparticles in PVA polymer films. The third order nonlinear optical susceptibilities were also calculated using the measured values of n_2 and β and it shows a significant third order nonlinear response. We investigated the thermo-optical nonlinearities of Ag nanoparticles with different concentrations in PVA polymer films. It was observed that the presence of the nanoparticles enhances both local and nonlocal (thermal) nonlinear responses of the dielectric matrix. On the other hand, the thermo-optical properties of the doped polymer films dramatically change as the concentration was increased. Our results suggest that thermal effects will play an important role in the development of photonic applications involving nanostructure materials and in the investigation of nonlocal nonlinear phenomena.

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