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Effect Of Cdte Nanoparticles On Linear And Nonlinear Optical Property Of Polyvinyl Alcohols PVA Film

Murtadha L. Sheqnab¹, Raad S. Alnayli²

^{1,2} Department of Physics, College of Education, University of AL-Qadisiyah, Qadisiyah, Iraq.

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Abstract:

Linear and nonlinear optical properties of Polyvinyl Alcohol thin film doped with cadmium telluride nanoparticles have been investigated experimentally. CdTe nanoparticles were produced in distilled water by pulsed laser ablation method under Nd-YAG laser at (100 mJ, 1064nm, 10ns, 6Hz, and 100 laser shots). AFM images were used to study the nanoparticles after ablation. XRD pattern and UV-Vis spectroscopy data were used to extract the structure and optical properties of films. Z-scan technique was employed to characterize of nonlinear optical properties of the films. The results of close-aperture z-scan data suggested that PVA/CdTe nanocomposite film included a nonlinear refractive index with a negative sign, meaning the occur of self-defocusing phenomenon. While, open-aperture z-scan data clearly suggested two-photon absorption as the dominant nonlinear absorption mechanism. The nonlinear property of PVA film was found increasing and strongly after added nanoparticles in them.

Keywords: Z-scan technique, Linear and Nonlinear optical properties, PVA polymer, CdTe NPs, Laser ablation.

1. Introduction

In the present time, the research on the synthesis and application of nanoparticles (NPs) has now been intensified due to its investment in many potential applications in biomedical, optical and electronic fields. Nanoparticles with typical dimensions of less than 100 nanometers have very special physical and chemical properties that are strongly dependent on their size and shape [1]. These important properties of nanoparticles, such as their chemical, electronic, mechanical and optical properties, clearly distinguish them from the characteristics of the bulk of these materials. The colloid nanoparticles in solutions were studied on a large scale because of their large third-degree nonlinear sensitivities and nonlinear optical response [2]. nanocrystalline materials have gained importance in recent years among the various nanoparticles available, because they represent a class of materials with exciting and new properties, and have wide technological applications such as photocatalysis, chemical remediation, photoinitiation of polymerization reactions, quantum dot devices and solar energy conversion [3]. In recent years, there has been an increasing interest in synthesis of II-VI semiconductor nanomaterials [4]. Nanocrystalline

semiconductor films appear as a new layer of photonic material due to their unique nonlinear visual effects and quantum confinement [5]. CdTe NPs are considered in preface of II-VI semiconductor material whose a possible advanced applications, ranging from microelectronics to fluorescent materials. This is due to the large synthesis capacity of its photovoltaic properties, which are realized by size, surface and morphology control of the particles in the quantum confinement regime [6]. CdTe nanoparticles have been a subject of numerous investigations. Because of high quantum efficiency and multicolor availability, CdTe nanoparticles can find applications in solid-state lighting, displays, optical communications, sensors, solar cell, as well as in biological imaging and detection [7]. The integration of semiconductor nanoparticles into functional polymers is a highly desirable approach to generating new materials for use in electronic optical devices, such as light emitting diodes and photovoltaic cells [8]. When nanoparticles are embedded in a polymer matrix, the linear and nonlinear optical properties of the nanocomposite films can be different from those of the pure polymer and nanoparticles. Polyvinyl alcohol (PVA) is a semicrystalline polymer, which may be a suitable host material due to its good thermostability, chemical resistance, high mechanical strength (film forming), water solubility, moderate and dopant dependent electrical conductivity along with its consideration among the best polymers as host matrix for CdTe NPs [9]. It is an important material with various applications, which is used in different field of science and technology. There are strong interactions between the polymer chains of PVA, which are attributable to the formation of hydrogen bonds between the hydroxyl groups. Metal NPs doped in polymers attracts great consideration; hence, the widened application goal offered by these hybrid materials. Liu et al. [10] showed that the crystal structure of PVA changes after the formation on a composite with NPs. For their application in optoelectronic, electrical, and optical devices, biomedical science, and so forth, main key points are selection of polymer-metal NPs combination, controlling the particles size, their concentration, and distribution within the polymer matrix [11-13].

Various methods have been developed for the preparation of colloidal solutions from NPs, such as chemical reaction, sol-gel, PVD, chemical vapor deposition (CVD), and laser cutting methods (PLA) [14]. Compared to conventional chemical methods, the PLA methods performed in liquids are clean and do not require any complex stimuli or sensitivities, and products usually require no additional purification. In addition, the size and shape of the NPs can be controlled almost by changing the laser energy and surrounding temperature in this way [15, 16]. Nonlinear optical techniques are important for materials research due to their high sensitivity to the molecular properties of the system [17-19]. A collective effort from physicists, chemists and material scientists is currently in progress to understand the fundamental relationships between the optical response and the molecular structure in polymers because it has specific properties such as high flexibility, and low density. Therefore, these materials have various industrial applications. As a result, one of the most significant ways to find material with noticeable nonlinear absorption coefficients or refractive index is based on NPs doped on polymers. The simplest method to measure the nonlinear optical properties of materials is Z-scan method. Z-scan is a well-established method for the determination of nonlinear refraction and absorption and has been widely used in material characterization since it can provide not only the magnitudes of real and imaginary parts of nonlinear susceptibility, but also their signs [20-23]. In this method, the sample is scanned along the propagation path of a focus the Gaussian laser [24]. The physical properties of a polymer are strongly dependent on the size or length of the polymer chain. In pconjugated organic compounds (polymers and oligomers), electron can move in large molecular orbitals.

In this study we used UV–Vis spectroscopy, XRD analysis, scanning, atomic force microscopy (AFM). Then single z-scan technique is employed to investigate the NLO properties of samples. We have experimentally investigated nonlinearities measurement including nonlinear absorption and nonlinear refractive index. Single-beam Z-scan technique performed with the 650 nm, laser light generated from a high power continues wave (CW) diode laser source, serving as the excitation beam.

2. Concept of Z-scan Technique and theoretical calculations

Z-scan is a technique that is particularly useful when the nonlinear refraction is accompanied by nonlinear absorption. This method allows the simultaneous measurement of both nonlinear refractive index and nonlinear absorption coefficient [25]. Basically, the method consists of moving a sample through the focal point of a positive lens and monitoring the changes in the far-field intensity pattern. Due to the light-induced lens-like effect, the sample has the tendency to recollimate or defocus the incident beam, depending on its z position with respect to the focal plane. By properly monitoring the transmittance changes through a small aperture at the far-field position (closed aperture), one can determine the amplitude of the phase shift ($\Delta\phi_0$) which its related with the difference in the normalized transmittance of the peak-valley in the normalized Z-scan curve (ΔT_{p-v}) according to the following relation [26]:

$$\Delta T_{p-v} = 0.406 \left| \Delta \phi_0 \right| \quad (1)$$

The nonlinear refraction index that determine from close aperture in Z-scan data is given by following relation [26]:

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

where λ is laser wavelength, $I_0 = 2P / \pi\omega_0^2$ is the input intensity of the laser beam at $z = 0$, where P is the power laser, ω_0 is the laser beam waist. and $L_{eff} = [1 - \exp(-\alpha L)] / \alpha$ is the effective thickness of the sample, where refer to α is the linear absorption coefficient, and L is the sample thickness.

On the other hand, by moving the sample through the focus of the lens and without an aperture at the detector (open aperture), can be estimate the nonlinear absorption coefficient from the Z-scan data at this method by relation [27]:

$$\beta = 2\sqrt{2} Z / I_0 L_{eff} \quad (3)$$

Where β is the absorption coefficient, Z is the one peak or one valley at the open aperture Z-scan curve.

3. Experimental details

The sample of CdTe NPs at high concentration was prepared by laser ablation method. Nd-YAG laser was used to ablated high purity CdTe target in distilled water. CdTe target was irradiated under 100mj pulsed energy, 1064nm wavelength, and 200 pulse number. The pulsed width and repetition rate of laser pulse were 10ns and 6Hz respectively. A 100mm focal length lens was used to focus the laser beam on the CdTe target. Height of liquid up the CdTe target was 4mm. The experimental setup for the ablation experiment is schematically shown in Figure 1. After prepared of colloid CdTe nanoparticles, part of it is taken and poured on a glass slide in order to test, as shown in Figure 2.

PVA films were prepared by dissolving 0.5g of commercial PVA powder in 10ml distilled water and stirred for 2h at 60C° temperature. One sample was fabricate without any CdTe NPs , and then 1ml of CdTe suspension was added into 1ml of PVA solution and again stirred for 1h at room temperature. To make

CdTe NPs doped PVA thin film, samples were then poured on a clean glass substrate and dried at the room temperature for 24h. The thickness of films was 10 μ m.

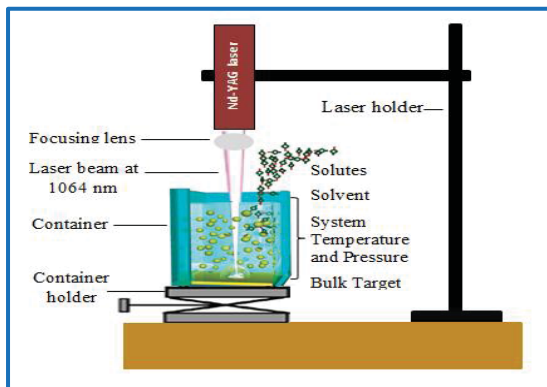


Figure 1. The experimental set-up to preparation of a colloid CdTe NPs by laser ablation method.

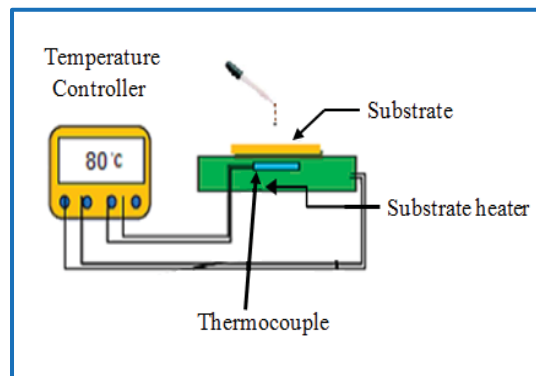


Figure 2. Schematic diagram to drop casting method.

The prepared films have been characterized by using double-beam UV-Visible spectrophotometer, model (SP-3000 Plus, OPTIMA) within the spectral range (200-1100 nm) was used to investigate the optical absorption spectra. X-ray diffraction pattern with system specifications (Shimadzu-XRD-6000, Company-Japan) with CuK α radiation at 1.5406 \AA wavelength in the range from (10 $^\circ$ - 80 $^\circ$), current 30 mA, voltage 40 KV, scanning speed (5 deg/min), were used to crystalline structure of this films. The atomic force microscopy (AFM) type (scanning probe microscope SPM-AA 3000, Angstrom Advanced Inc., USA) was used to analyze of the topography and also to determine diameter of CdTe nanoparticles. The nonlinear optical properties of pure PVA and PVA/CdTe nanocomposite films were measured by using the Z-scan technique. Based on the method developed by Sheik-Bahae et al. (2000). The experimental setup of Z-scan experiment is shown in Figure 3. The excitation source in our experiment was diode laser within a continuous wave (CW) at 650 nm wavelength. In the experimental setup of Figure 3, the radius of laser spot was 0.4 mm, the laser beam was focused to a sample by a 15 cm focal length lens. The output beam power of the laser was 50 mW. A power meter were used to measure the incident and transmitted power of laser beam. Movement of sample in the experiment was done using a micrometer translating stage. The distance between the lens focal point as the origin and power meter was changed from -5 cm before of focal lens and +5 cm after that during the experiment. The pinhole was 0.7 mm in diameter.

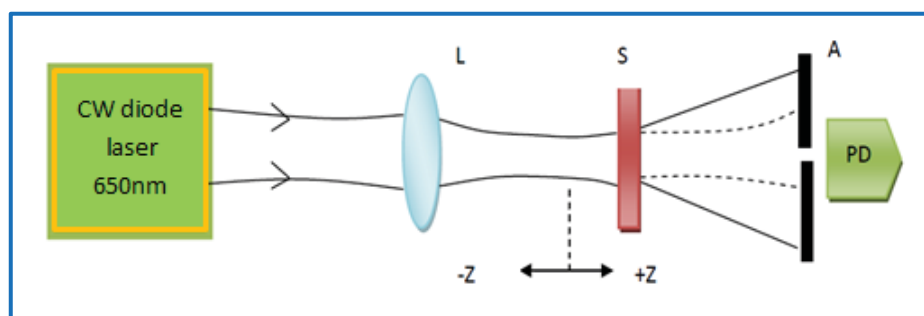


Figure 3. Schematic diagram of experimental close Z-scan setup.

4. Result and Discussion

A. AFM analysis

AFM images of CdTe nanoparticle suspensions in distilled water are presented in Figure (4a, b). For taking AFM image a drop of the suspension containing nanoparticles is deposited and dried on a clean glass as we mentioned earlier in the experimental set-up which shown in Figure 2. As can be seen from Figure 4a that CdTe nanoparticles are formed of a spherical shape. Beside each image in Figure 4, the particle size distribution of CdTe nanoparticles, obtained from AFM analysis is plotted using measurement software, where average size of CdTe nanoparticles was 47 nm.

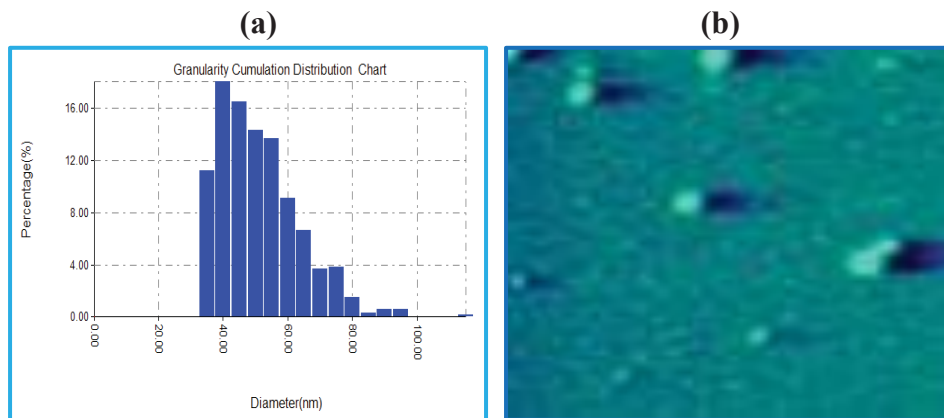


Figure 4. AFM analyze; (a) Image of CdTe NPs, (b) Size distribution of CdTe NPs diameters.

B. XRD analysis

Figure 5. shows the x-ray diffraction pattern of both the pure PVA and PVA/CdTe nanocomposite films. XRD pattern of pure PVA exhibit that a film was amorphous nature with a broad diffraction peak at $2\theta = 19.9^\circ$ which corresponds to semi crystalline nature of PVA [28]. While, XRD pattern of PVA/CdTe nanocomposite film exhibit a peak at $2\theta = 23.36^\circ$ and 39.06° corresponds to hkl plane of (111) and (220), which matches well with the standard data of JCPDS Card No. 15-0770 and it confirms cubic structure of CdTe [29,30]. On the other hand the region of XRD concerning the semi crystalline of PVA, has been changed according to the CdTe which additive in the polymer matrix. Certainly in the doped film the peak of PVA has been found to be increased in broadness and decreased in intensity, which indicate an increasing in the amorphous region of PVA in the doped films after doping with CdTe NPs .The average crystalline size of the nanocomposite film was calculated using Debye Scherer equation [31]:

$$D = k \lambda / \beta \cos\theta \quad (4)$$

Where, D is the average particle size, K is a geometric factor (which is equal to 0.94), λ is the wavelength of X-ray (1.5406\AA), β is the full width half maximum of the diffraction peak. The calculated nanocrystallite size is found to be 23.70 nm of PVA/CdTe nanocomposite film.

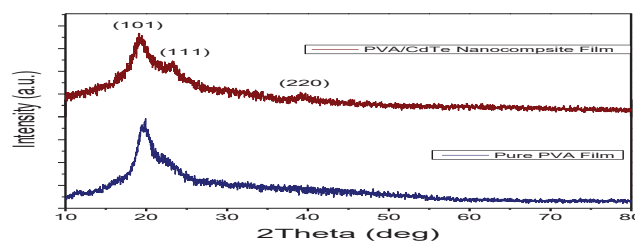


Figure 5. XRD pattern of pure PVA and PVA/CdTe nanocomposite films

C. UV-Visible measurement

The UV-Vis absorption spectra of the pure PVA and PVA/CdTe nanocomposite thin films are shown in Figure 6. As clear from Figure 6, the pure PVA thin film exhibited low absorbance at UV region, and no absorption peak was found. High absorbance and prominent peak was observed after doping nanoparticles in PVA film. The absorption edge shifted towards higher wavelength side, indicating the decrease in the optical band gap for the PVA polymer film under effect the CdTe nanoparticles. From the spectra, it is observed that the sharp increase in absorbance of the PVA/CdTe nanocomposite thin film is an indication of good crystalline nature of the film [32].

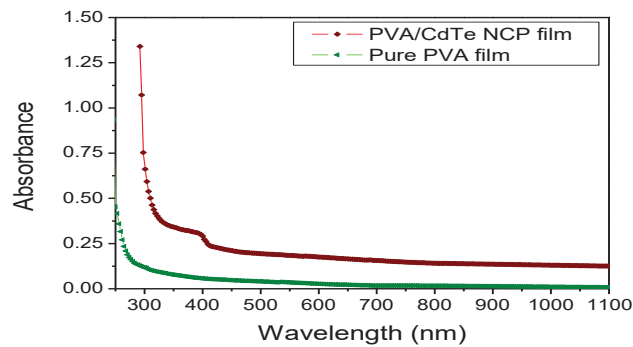


Figure 6. UV-Vis absorption spectra of pure PVA and PVA/CdTe nanocomposite thin films.

The optical absorption coefficients of films are evaluated by depending on the absorbance data using the relation [33]:

$$\alpha = 2.303A/d \quad (5)$$

where α is the absorption coefficient, A is the absorbance, and d is the thickness of films. Figure 7 presents the optical absorption coefficient of pure PVA and CdTe NPs doped PVA films. As can be seen from Figure 7 the absorption coefficient of PVA film was increased after doping nanoparticles in them. This increased in absorption coefficient is indicate to PVA under the influence of CdTe nanoparticles [34].

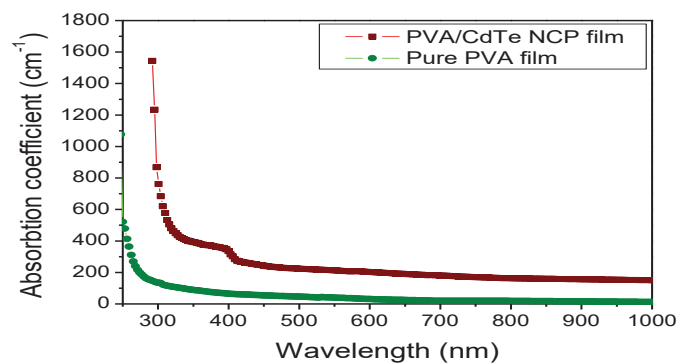


Figure 7. Optical absorption coefficient of Pure PVA and PVA/CdTe nanocomposite films.

The absorption peak, appeared in UV range, is due to the energy gap of films in this area. The position of the absorption edge was determined by extrapolating the linear portions of α versus $h\nu$ curves to zero absorption value. It is clear from Figure 6 that the band edge was decreased after doping nanoparticles in the structure of film. The absorption edge shifted towards higher wavelength side, indicating the decrease in the optical band gap for the PVA polymer film.

The most used method for estimation of the band gap from optical measurement by using Tauc relation [35, 36]:

$$\alpha h\nu = B (h\nu - E_g)^r \quad (6)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, B is a factor that depends on transition probability and can be assumed to be constant within the optical frequency range, E_g is the optical band gap of the samples, and index r is related to the distribution of the density of states, which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of electronic transition. By taking $r = 1/2$ which selected by fitting method as seen occur a direct transition. Hence the optical band gap of samples were deduced from the intercept of the extrapolated linear part of the plot of $(\alpha h\nu)^2$ versus the photon energy and extrapolating the straight line to the energy axis of the graph to the $h\nu$ axis, that is, at $\alpha = 0$. Band gap energy of pure PVA film is extracted to be 4.1 eV. While, Band gap energy of PVA/CdTe nanocomposite film is found to be 3.27 eV. As can be seen from Figure 8, the energy gap of PVA is decreased noticeably after doping nanoparticles, which is the effect of CdTe nanoparticles dopant. This change in band gap of PVA polymer due to doped nanoparticles is very important in physical properties, which done of improve them, and this agreement with [37, 38].

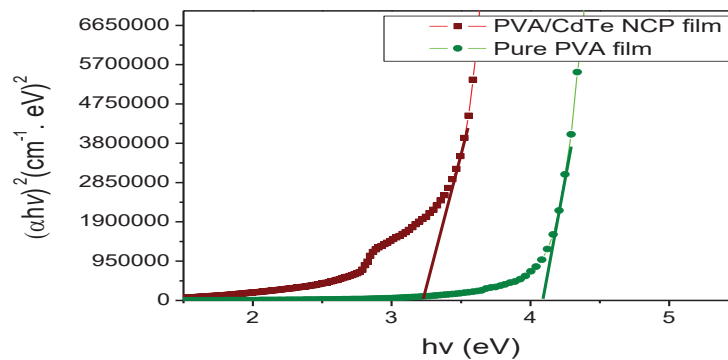


Figure 8. $(\alpha h\nu)^2$ versus photon energy gap varies of pure PVA and PVA/CdTe nanocomposite films.

D. Nonlinear optical properties measurements

Pure PVA film has been calibrated before doping CdTe nanoparticles in them. The transmittance curve of pure PVA film was a low and there is no presence of any peak or valley i.e. the nonlinear response of the pure PVA film is very weakly, as clear from open and close Z-scan data in Figure 9 and 10 respectively. On the other hand, Figure 9 showed the closed aperture Z-scan data for PVA/CdTe nanocomposite films. It clear from Figure 9, the peak followed by a valley in normalized transmittance results indicates that the sign of the refractive index nonlinearity is negative, i.e. self-defocusing behavior [39].

Moreover, the nonlinear absorption was evaluated by open-aperture z-scan technique. The gained data curves in figure 10 shows PVA/CdTe nanocomposite film has a positive of nonlinear absorption coefficient, since they have a significant valley. This result suggested that this nonlinearity is mainly due to two-photon absorption phenomena [40]. The nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) of PVA/CdTe nanocomposite film have been estimated using equations (2) and (3), where found of the values are $-1.38 \times 10^{-7} \text{ cm}^2/\text{mW}$ and 3.81×10^{-5} respectively.

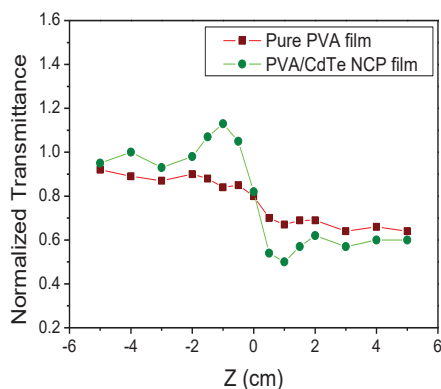


Figure 9. Cloed-aperture Z-scan curve of pure PVA and PVA/CdTe nanocomposite film.

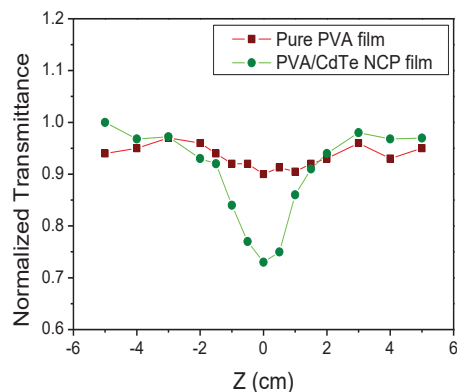


Figure 10. Open-aperture Z-scan curve of pure PVA and PVA/CdTe nanocomposite film.

From previous observations it turns out that After doped CdTe NPs in PVA matrix, the nonlinear optical properties of PVA film is improved, where become characterized with a strong nonlinear property. Therefore, these nanocomposite films offer prospects of application as efficient optical limiters to protect light sensitive devices from the possible damage on exposure to high intensity radiation.

5. Conclusion

The pure PVA and PVA/CdTe nanocomposite films were prepared successfully by drop casting method. CdTe NPs prepared by laser ablation have been studied through AFM microscopy. XRD pattern showed the effect the doping nanoparticles on the structure of PVA film where observed appear a new peaks attributed to CdTe. Uv-Vis spectroscopy showed a clear change in absorbance peak of PVA film after doped nanoparticles, and the band gab of PVA film was decreased due to effect nanoparticles. The results of close-aperture z-scan data suggested that PVA/CdTe nanocomposite film included a nonlinear refractive index with a negative sign, meaning the occur of self-defocusing phenomenon. While, open-aperture z-scan data clearly suggested two-photon absorption as the dominant nonlinear absorption mechanism. The nonlinear property of PVA film was found increasing and strongly after added nanoparticles in them.

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