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The nonlinear optical properties of Epoxy/Alumina Nanocomposites

Ahmed H. Wheeb **Zainab F. Mahdi** and **Rawaa A. Faris**

Institute of Laser For Postgraduate Studies, University of Baghdad, Baghdad, Iraq

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Abstract: Linear and nonlinear optical properties of epoxy/ Al_2O_3 nanocomposites system were studied for epoxy neat and (0.5, 1.5, 3, and 5) % Al_2O_3 nanocomposites.The band gap of epoxy and its nanocomposites was obtained at these weight ratios. Nonlinear optical properties experiments were performed using Q-switched Nd:YAG laser z-scan system.These experiments were carried out for different parameters: wavelengths (1064 nm and 532 nm), laser intensities (0.530, 0.679, and 0.772) GW/cm2 and weight ratio of Al_2O_3 nanocomposites. The results showed that the band gaps were decreased with increasing the weight ratio of nanoalumina except at 5wt% and the nonlinear refractive index coefficient is directly proportional to the incident intensities while opposite for the nonlinear absorption coefficient. Different types of nonlinear absorption coefficients were given .One, two and three photons absorption according to band gap and laser photon energy were appeared. So that epoxy/ Al_2O_3 nanocomposites can be used as a promising nonlinear device.

Introduction

The growing demand to nanomaterials is due to the fact that new chemical and physical properties are attainable when nanosized fillers added into polymer matrixes where a single molecule or the same material without nanofiller does not show such an advantages.In the past decades an extensive research activities have been devoted on incorporating polymers with nanoparticles since polymer-based nanocomposites showed much better thermal and mechanical properties compared to the polymer matrixes having micron sized particles . This is due to the effect of the unique nature of the nanosized filler on the bulk properties of polymer-based nanocomposites [1] .In addition, at the effect of pump laser, the enhancement of electron cloud deformation and optical Kerr effect makes the nanometer materials have large third-order optical nonlinearities than that of the bulk ones[2]. This change in refractive index leads to self-focusing or defocusing of light beam within materials with appreciable n2 values. The typical transmission with peak-valley shape dependent on the change in refractive index acts like an ON–OFF switch. This indicates that these quantum structures can be used for nonlinear device. At last, the z-scan technique was employed tomeasure the sign and the magnitude of the nonlinear refraction index and multi-photon absorption coefficient of the sample. Such materials are very promising for nonlinear device[3]. The nonlinear optical properties of nanocomposites are analysed by the single beamz-scan technique, which is based on the intensity-dependent refractive index. The refractive index of the material originates from the third-order.susceptibility of the material, which cannot be neglected when the incident light intensity is high. The z-scan method provides a sensitive and straightforward method for the determination of the nonlinear refractive index and the nonlinear absorption coefficient. The technique has been widely employed for characterizing the optical nonlinearity of nanomaterial. The relative on-axis transmittance of the sample measured (at the small aperture of the far-field detector) is given by[4]:-

$$T(z, \Delta\Phi o) = 1- \frac{4\Delta\Phi o\ Z/Zo}{[(Z^2/Zo^2)+9][(Z^2/Zo^2)+1]} \quad ..(1)$$

where T is the transmittance through the aperture, which is a function of the sample position Z, ΔΦo is the on-axis phase change given by the following formula[5]:-

ΔΦo=ΔTpv/0.406(1-S)0.25 (2)

S: the fraction of beam transmitted through the aperture.

the nonlinear refractive index, is calculated from the peak to valley difference of the normalized transmittance by the following formula[6]:-

n2 = ΔΦo/Io Leff k (3)

k = 2π /λ , λ ,is the wavelength of the beam

Leff: - the determined from the following formula[7]:-

Leff= (1-e-αoL) /αo (4)

Where,

L: - the sample length,

αo :- linear absorption coefficient

In this work, nonlinear optical properties experiments were performed using Q-switched Nd:YAG laser z-Scan system. The nonlinear optical properties were represented by nonlinear refractive index and nonlinear absorption coefficients. These experiments were carried out for different parameters.

Experimental

A. Material Preparation

The sample is epoxy neat and their nanocomposite which consist of resin (LEYCO –POX 103)and hardener which was added to resin in weight ratio 1:2(hardener: resin) and thus the chemical bonding and crosslinking was formed within the epoxy . Nanoalumina with particle size equal to < 50 nm prepared by (SIGMA-ALDRICH)was added in different weight ratio (0.5%, 1.5%, 3%, and 5%).

Sample Testing

Linear optical properties testing

The linear optical properties testing were achieved by measuring the linear refractive index, linear absorption coefficient and band gap by using spectrophotometer..

The nonlinear optical properties testing

The nonlinear optical properties testing by z-Scan technique which include the nonlinear refractive index and nonlinear absorption coefficient. The z-Scan technique is presented and measurements were done at 1064nm and at 532nm for different weight ratios of Al_2O_3 nanoparticles embedded in epoxy system. Fig. (3) Shows the set-up of the z-scan system.

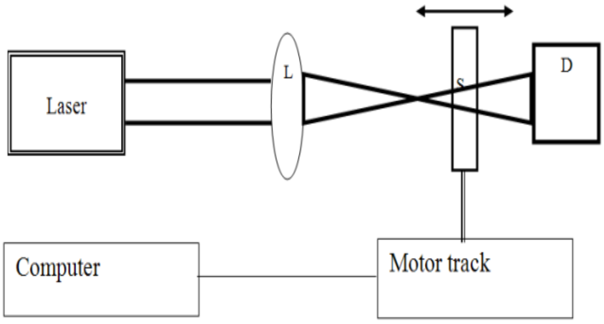

Fig. (1): schematic diagram of z-Scan experimental setup: L-Lens ,S-Sample, and Detector.

Results and Discussion

Linear Optical Properties testing:-

UV-VIS-NIR absorption spectrum was obtained for epoxy and their nanocomposites as shown in Figure 2. Epoxy neat has high absorption at UV region and high transparent at visible and NIR regions. Notice thatthe absorption of nanocomposites are increased with increasing the weight ratio of the nano- Al_2O_3 filler at 1064 nm and 532 nm. Figure 2 shows the absorption photon-energy spectra of epoxy/ Al_2O_3 nanocomposites at different weight ratio of nano Alumina. The intercepts of tangents are used to estimate the band gap energies, which are 2.6, 2.2, 1.9 and 2 for (0.5, 1.5,3, 5) wt% of nano Al_2O_3 weight ratio, respectively. The absorption edge shifts to low-energy side with increasing Alumina weight ratio from (0.5- 3) %. This might be attributed to the increase in the size ofAlumina nanoparticles in the epoxy. However, the band gap energy of 5 wt% is higher than that of 3wt%, which suggests that alumina nanoparticles in 5wt% should be smaller than those in 3wt %. It can also be proved by the simple linear optical spectra showing a red shift in the absorption peak as the alumina weight ratio increase, at 5wt% the blue shifts behavior can be shown in Figure 3. This because the nanoparticles themselves could act as conductive junctions between the polymer chains that resulted in an increase of the electrical conductance of the composites in which leads to a decrease in their optical band gap energy. This result is in agreement with the result reported by G. Ouyang et al., [8].

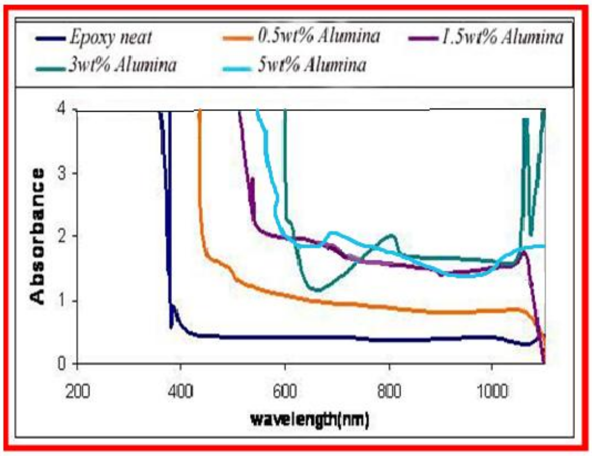

Fig. (2): UV-VIS-NIR absorption spectrum of the epoxy neat and their nanocomposites

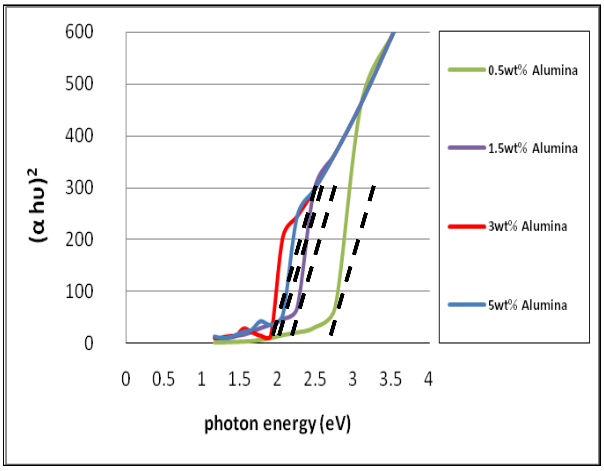

Fig. (3): Absorption-photon-energy spectra for epoxy/Al_2O_3 nanocomposites at different weight ratio of nano Al_2O_3 .

Nonlinear Optical Properties testing

The nonlinear properties were measured by extracting the nonlinear refractive index coefficient (n2) by closed-aperture z-Scan measurements and nonlinear absorption coefficient (β) by open-aperture z-Scan measurement with different weight ratio (0.5, 1.5,3 and 5) wt% of Al_2O_3 nanoparticles. Closed –and open-aperture z-Scan measurements are performed at different excitation intensities (0.530, 0.679 and 0.772) GW/cm2 at 532 nm and 1064 nm to evaluate the nonlinear optical response.

Nonlinear Refractive Index Coefficient (n2) measurements

The closed aperture z-Scan technique allowed us to determine the sign and magnitude of the nonlinear refractive index. In order to extract the pure nonlinear refraction part,the data of a closed-aperture z-Scan measurements were divided that of an open aperture z-Scan measurements.

The Effect of nano Al_2O_3 Weight Ratio on the Sign of the Nonlinear Refractive Index Results

The normalized transmittances of z-Scan measurements as a function of distance from the focus of the Gaussian beam at applied incident laser were done. Figures (4, 5 and 6) show these measurements for epoxy and their nanocomposites at 532nm for different intensities (0.530, 0.679 and 0.772) GW/cm2 respectively.

The shape of the z-Scan results for the epoxy is semi flat, which suggests that the epoxy neat has a small nonlinear optical effect, so the large nonlinear responses observed in the samples are from the nano alumina. The transmittance was increased directly with increasing weight ratio for the same intensity and wavelengths accept at 5% weight ratio due to aggregation [6].

The behavior of the closed aperture z-Scan of epoxy and their Nanocomposites at 1064nm can be shown in Figures (7,8 and 9). All experiments were performed under the same conditions of 532nm.

From the previous figures there are two signs of nonlinear refractive index. The first one a negative z-Scan profile. It is beginning far from the focus (*z* <0), the beam intensity is low and nonlinear refraction is negligible, in this condition, the measured transmittance remains constant (i.e., *z*-independent). As the sample approaches the beam focus, intensity increases, leading to self lensing in the sample tend to collimate the beam on the aperture in the far field, increasing the transmittance measured at the iris position. After the focal plane, the self-defocusing increases the beam divergence, leading to a widening of the beam at the iris and thus reducing the measured transmittance. Far from focus (z > 0), again the nonlinear refraction is low resulting in a transmittance z-independent [9].The second one behavior of nonlinear refractive index is positive nonlinear refractive index. It is starting the z-Scan far from the focus. The beam intensity is low and negligible nonlinear refraction occurs, the transmittance remains relatively constant near this sample position. As the sample is brought closer to focus, the beam intensity increases leading to self-focusing. This positive NRI moves the focal point closer to the lens causing greater beam divergence in the far field. Transmittance through the aperture is reduced. As the sample is moved past the focus, self-focusing increasingly collimates the beam resulting in enhanced transmittance through the aperture. Translating the sample further toward the detector reduces the intensity to the linear regime. Reading the data right to left, a valley followed by peak is indicative of positive nonlinear refractive index[10].

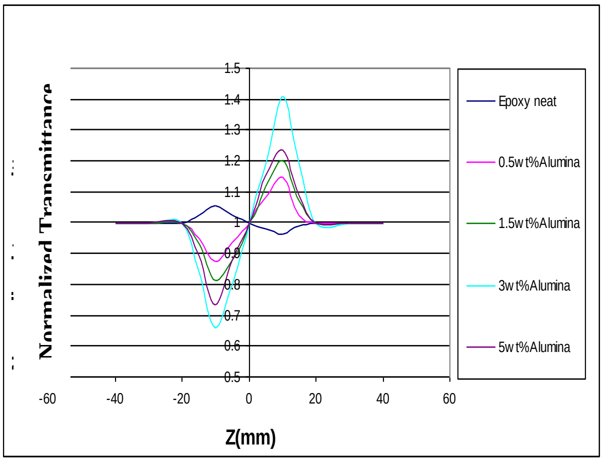

Fig. (4): Closed-aperture of different weight ratio of nanoAl_2O_3 for 0.530GW/cm^2 at 532nm.

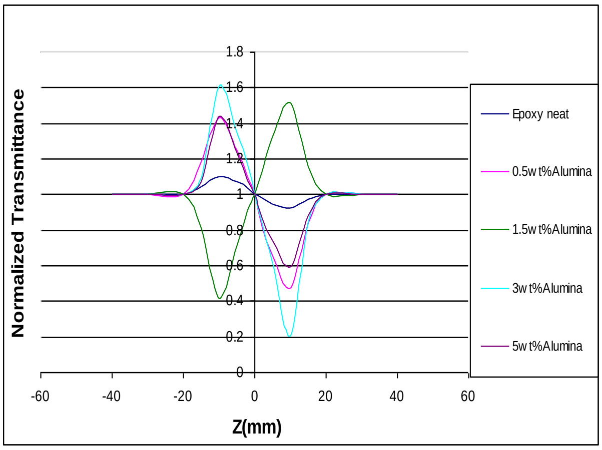

Fig. (5): Closed-aperture of different weight ratio of nanoAl_2O_3 for 0.679GW/cm^{2}at 532nm

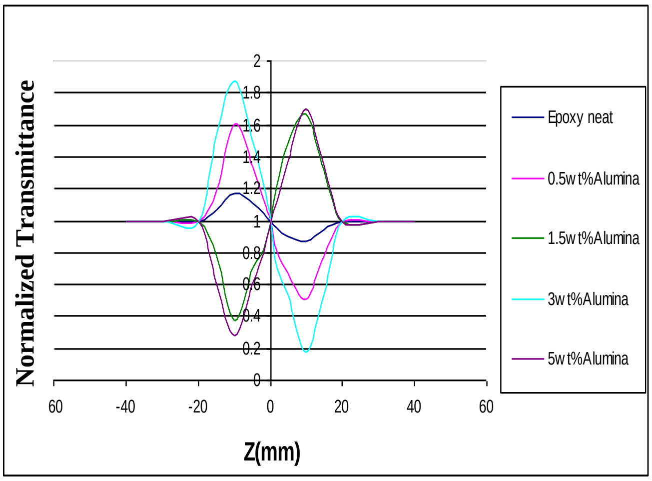

Fig. (6): Closed-aperture of different weight ratio of nanoAl_2O_3 for 0.772 GW/cm^2 at 532nm.

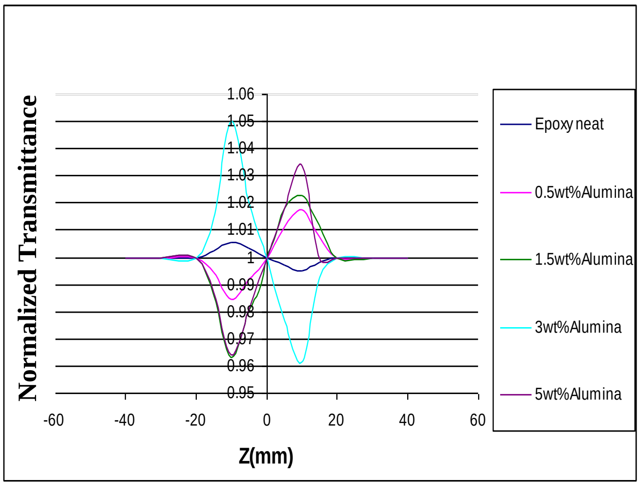

Fig. (7): closed-aperture of different weight ratio of nanoAl_2O_3 at 0.530 GW/cm^2 at 1064nm.

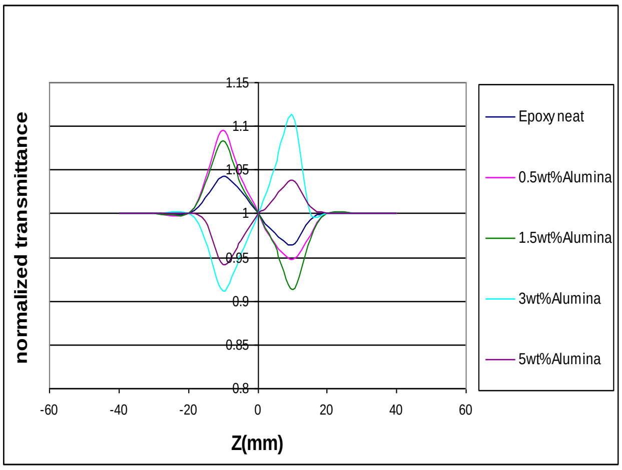

Fig. (8): closed-aperture of different weight ratio of nanoAl_2O_3 at 0.679 GW/cm^2 at 1064nm.

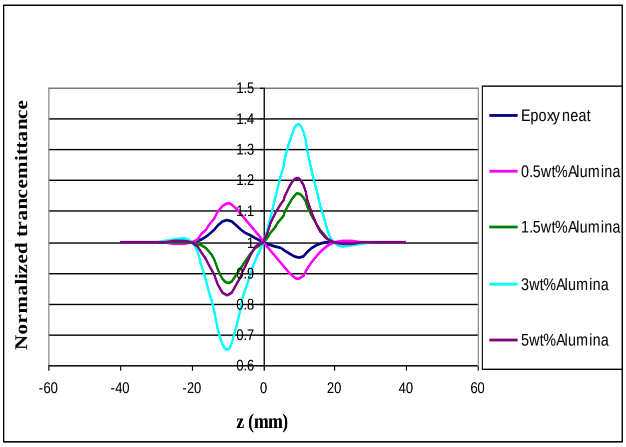

Fig. (9): closed-aperture of different weight ratio of nanoAl_2O_3 at 0.772 GW/cm^2 at 1064nm.

The Effect of the Intensity and Wavelength on the Sign of the Nonlinear Refractive Index Results

Figures (9, 10, 11, 12 and13) represented closed aperture z-Scan of (epoxy neat, 0.5, 1.5, 3 and 5wt %) respectively at (532, 1064)nm wavelengths and different intensities. As the sample moves through the beam focus (at z = 0), self –focusing or self-defocusing modifies the wave front phase, thereby modifying the detected beam intensity[11]. The differences between two wavelengths are the high transmittance at 532nm than 1064 nm at the same intensity. As seen from figures the transmittance of all samples were enhanced with increasing the intensity. Due to at the intensity increases, population of electrons saturates the conduction band thus blocking further excitation from valance band, hence transmission through the sample increases[12].

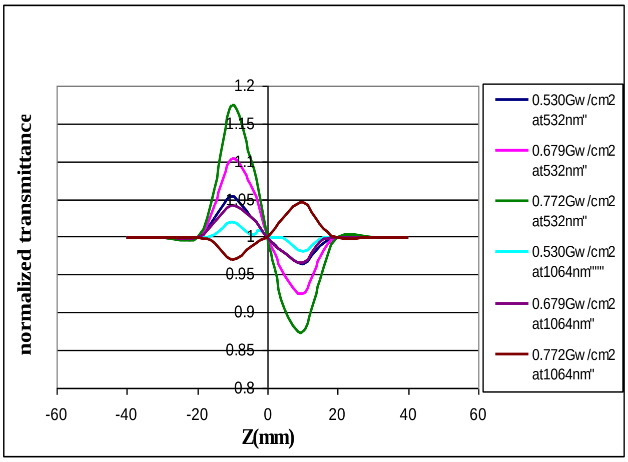

Fig. (10): The closed-aperture z-Scan of epoxy neat at different intensities for different wavelengths

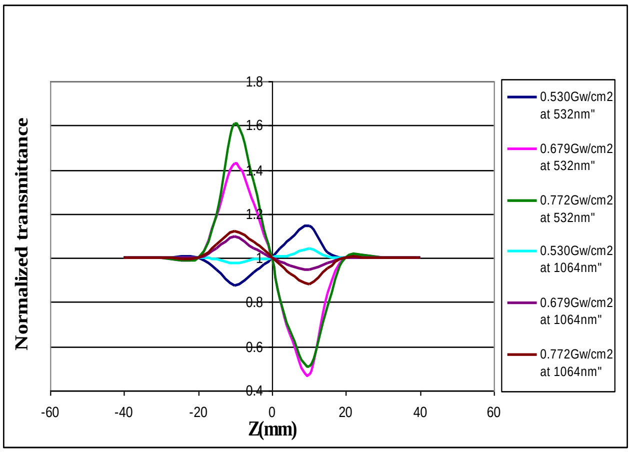

Fig. (11): The closed-aperture z-Scan of 0.5wt% Alumina at different intensities for different wavelengths

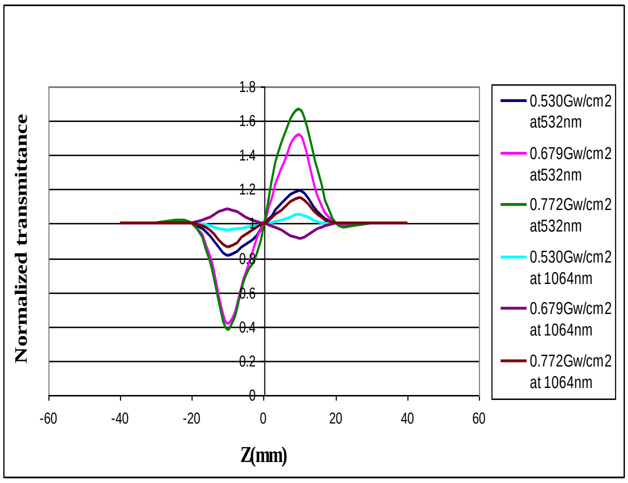

Fig. (12): The closed-aperture z-Scan of 1.5wt% Alumina at different intensities for different wavelengths

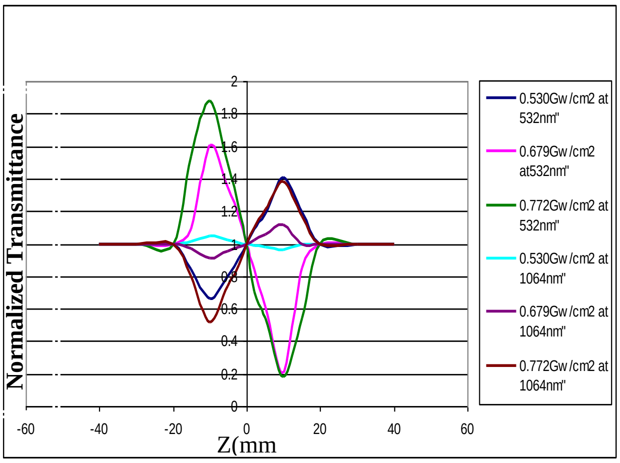

Fig. (13): The closed-aperture z-Scan of 3wt% Alumina at different intensities for different wavelengths

The Effect of Nano Al_2O_3 Weight Ratio on the Magnitude Of the Nonlinear Refractive Index Results

The magnitude of nonlinear refractive coefficient is affected by many reasons as variation in concentration, dielectric confinement effect, aggregation (particle-particle interaction) of Al_2O_3 nanoparticles and the state of epoxy. Figures (14) and (15) represented the relation between nonlinear refractive index with epoxy neat and their nanocomposites for different intensities at 532 nm and 1064 nm.The dependency of the magnitude of nonlinear refraction n2 on the weight ratio of Al_2O_3 nanoparticles is shown in Figures (16) to (17). The figures show that there is an enhanced optical nonlinearity in the 0.5%,1.5%, 3% sample and a reverse decrease in 5%.There exists an optimum weight ratio of 3wt% Al_2O_3 precursor in the nanocomposites, demonstrating the strongest response for nonlinear optical behavior. If the Al_2O_3 nanoparticlesweight ratiois less than or equal to 3%, n2 increases linearly as the Al_2O_3 nanoparticles weight ratio increases. However, a further increase in Al_2O_3 nanoparticles content to 5% weight ratio of Al_2O_3 nanoparticles provides a decrease, n2 deviates from the linear growth this because , the quantum confinement effect decreases obviously due to large aggregation of nanoparticles in 5% weight ratio of Al_2O_3 nanoparticles**.**These might be reasons why nonlinear optical response of 5% Al_2O_3 nanoparticles is decreased[6].

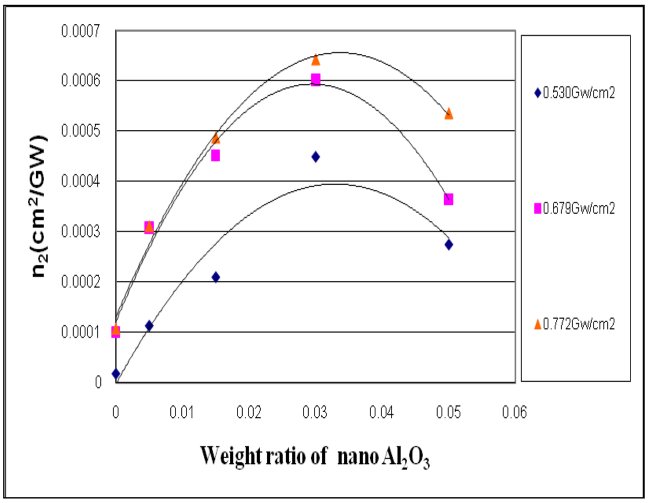

Fig. (15): The relation between n_2 and different weight ratio of nano Al_2O_3 at 532nm

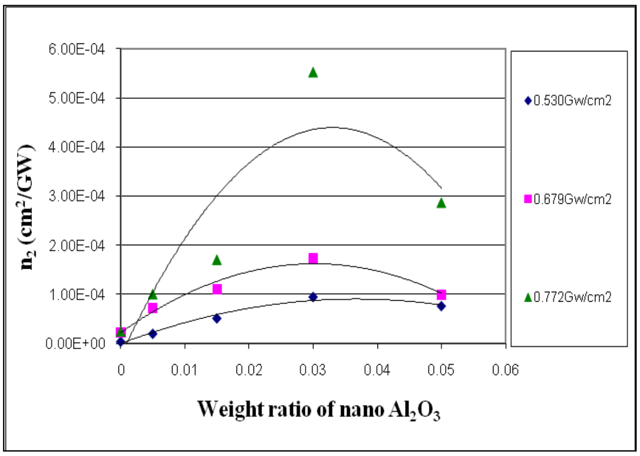

Fig. (16): The relation between n_2 and different weight ratio of nano Al_2O_3 at 1064nm

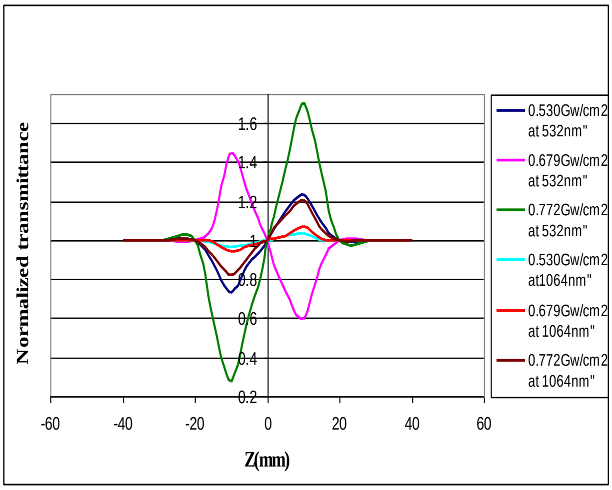

Fig. (14): The closed-aperture z-Scan of 5wt% Alumina at different intensities for different wavelengths

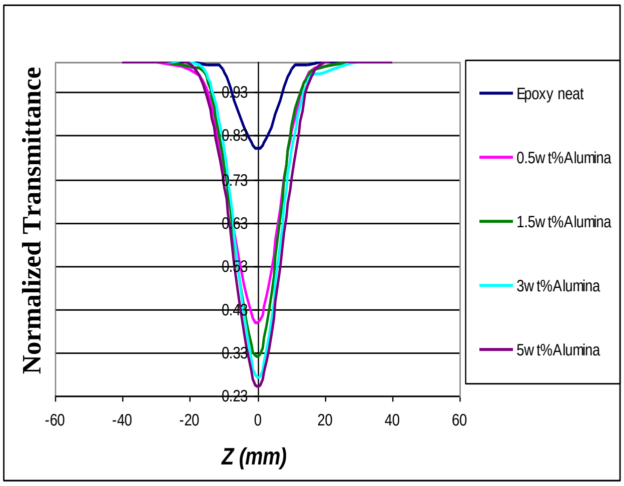

Fig. (17): The open-aperture z-Scan of different weight ratio of nanoAl_2O_3 for 0.530GW/cm^{2}at 532nm

Nonlinear Absorption Coefficient Results

The magnitude of nonlinear absorption coefficients ***β*** of epoxy neat and their nanocomposites were estimated by performing the open aperture z-Scan technique. ***β*** is related to the imaginary part of the third-order optical susceptibility $\chi(3)$.Open aperture z-Scan that performed in this study exhibited a reduction in the transmission about the focus of the lens.

The Effect of Al_2O_3 Weight Ratio on Nonlinear Absorption Coefficient Results

The normalized transmittance curves of epoxy neat and different weight ratio of Al_2O_3 at 532nm are shown in Figs.(18-20) for different intensities.

As shown in the figures, the depth of reduction changes along with variation of the on-focus intensity and Al_2O_3 nanoparticles weight ratio, the nonlinear absorption coefficient is often enhanced because of increasing particle weight ratio and confinement beside the quantum confinement effect .In fact, nanoparticles have special surface structure and high surface activity, so their optical properties will have an obvious with surrounding environment. In all Figures of the open aperture z-Scans curves, the valley depth in the open aperture z-Scan trace enlarges gradually as the weight ratio of the Al_2O_3 nanoparticles increases. The optical properties of nanocomposites have distinct difference from those of epoxy neat.

The surface states are easily formed due to a lot of defects in the surface of Al_2O_3 nanoparticles, which makes an important contribution to nonlinearity of nanocomposites. Due to the larger interface of Al_2O_3 nanoparticles, when it is wrapped with epoxy neat possessing smaller dielectric coefficient, the electric charge interaction between them is strong so that the dielectric confinement effect can be formed in the nanoparticles surface.

This effect is a surface polarization depending on the permittivity ratio between particles and surrounding medium[6]. The effect of 1064nm wave length at different weight ratio of Al_2O_3 filler for different intensities was shown in Figures (21-23) .The energy of laser photon at 532 nm and 1064 nm is 2.33 eV and 1.1625 eV, respectively.

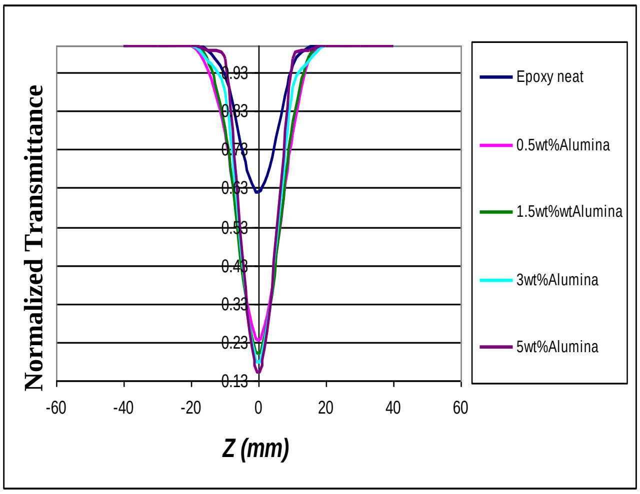

Fig. (18): The open-aperture z-Scan of different weight ratio of nanoAl_2O_3 for 0.679GW/cm^2 at 532nm

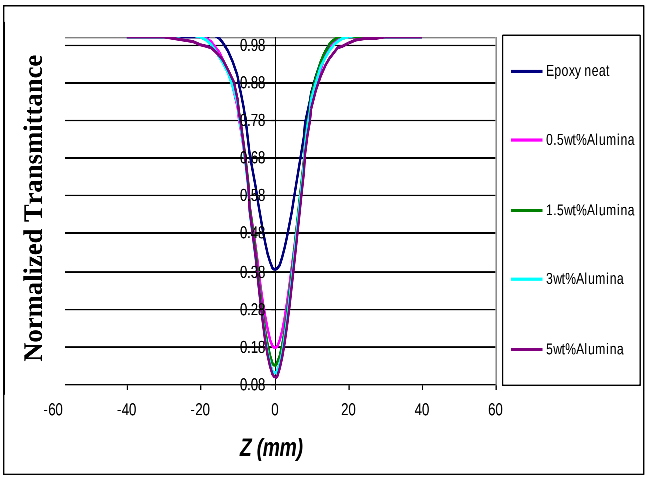

Fig. (19): The open-aperture z-Scan of different weight ratio of nanoAl_2O_3 for 0.772 GW/cm^2 at 532nm

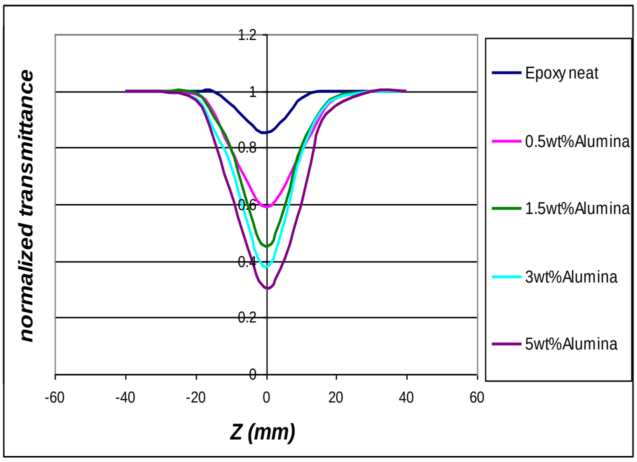

Fig. (20): The open-aperture z-Scan of different weight ratio of nano Al_2O_3 for 0.530 GW/cm^2 at

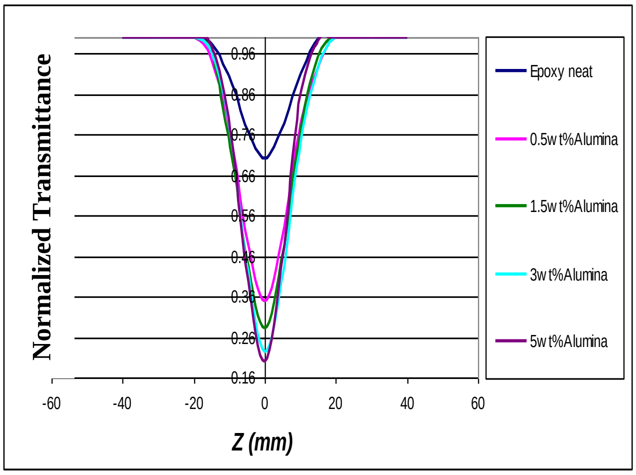

Fig. (21): The open-aperture z-Scan of different weight ratio of filler for 0.679 GW/cm^2 at 1064nm

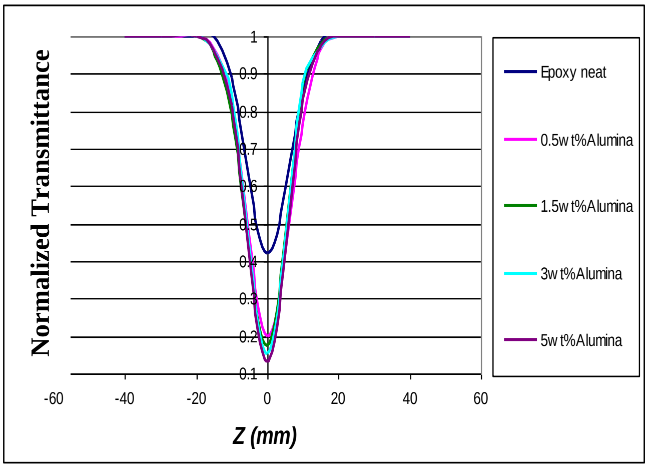

Fig. (22): The open-aperture z-Scan of different weight ratio of nanoAl_2O_3 for 0.772 GW/cm^2

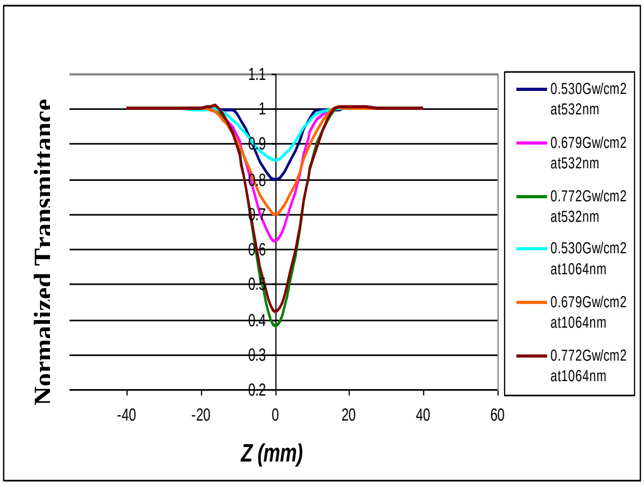

Fig. (23): The open-aperture z-Scan of Epoxy neat at 532 nm and 1064nm for different intensities.

In order to cross the band gap of the nanocomposites, it must need several photons in some types of nanocomposites as at Table (1)

Table (1): Band gap, wavelength and different type absorption transition for epoxy/ Al_2O_3 nanocomposites.

Al_2O_3	*Band gap (eV)*	*Wavelength (nm)*	*Transition type*
0.5%	2.6	532	TPA
		1064	3PA
1.5%	2.2	532	1PA
		1064	TPA
3%	1.9	532	1PA
		1064	TPA
5%	2.0	532	1PA
		1604	TPA

The Effect of the Intensity and Wavelength on the Nonlinear Absorption Coefficient Results

z-Scan curves were recorded at two different wavelengths 532nm and 1064nm for investigating the nonlinear absorption coefficients of epoxy neat and their nanocomposites. The effect of nonlinear absorption in epoxy neat and their nanocomposites at 532 nm and 1064 nm is shown in Figures (24-27) at different intensities.

The magnitude of the nonlinear absorption coefficient (***β***) is very depending on the intensity and wavelengths, where the (***β***) is inversely proportional with the intensity. The observed effect shown in previous figures are attributed to a thermal nonlinearity resulting from the amount of absorption of radiation at 532 nm and 1064nm. Localized absorption ofa tightly focused beam propagating through anabsorbing medium in epoxy/AlO3nanocomposites produce different spatial distribution of temperature in the samples and consequently, difference of spatial variation of refractive index, acts asathermal lens. Generallythe measurements of the normalized transmittance versus sample position, where the transmittance are sensitive to the nonlinear absorption as a function of input intensity [13]. The transmittance behavior of all previous figures is started linearly when the sample is located far from the beam waist, where the beam intensity is low; the transmission through the aperture is normalized to unity. As the sample is shifted closer to the waist, the induced nonlinear absorption and the transmittance curve begins to decrease until it reaches the minimum value (Tmin) at the focal point, where Z=0 mm. Afterward, the transmittance begins to increase toward the linear behavior at the far field of the waist. In the open-aperture z-Scan, the nonlinear behavior of the transmission curves in good agreement with the result reported by Dement[13]. In the focal plane where the intensity is greatest, the largest nonlinear absorption is observed.

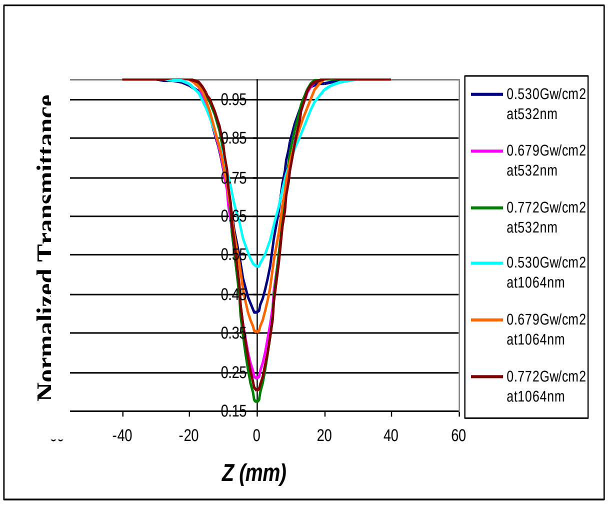

Fig. (24): The open-aperture z-Scan of 0.5wt% Alumina at 532 nm and 1064nm for different intensities.

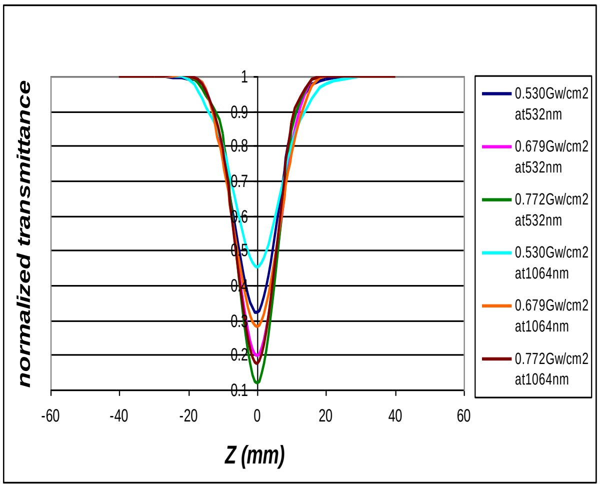

Fig. (25): The open-aperture z-Scan of 1.5wt% Alumina at 532 nm and 1064nm for different

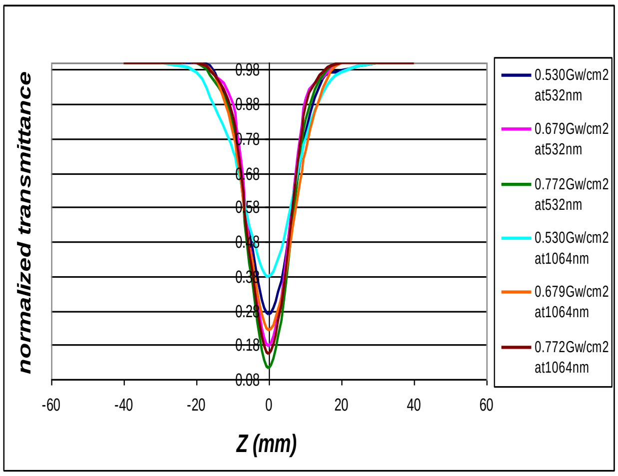

Fig. (26): The open-aperture z-Scan of 3wt% Alumina at 532 nm and 1064nm for different intensities

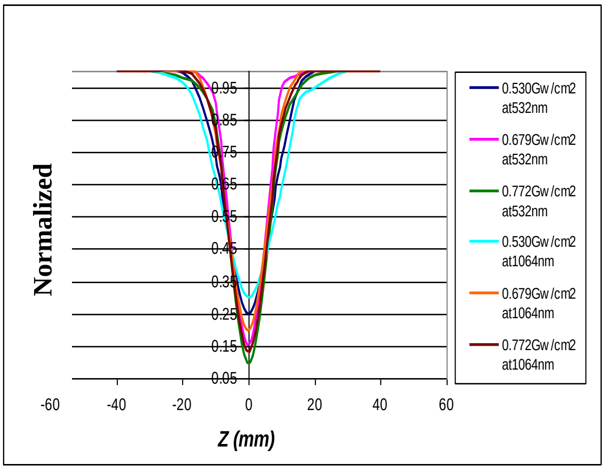

Fig. (27): The open-aperture z-Scan of 5wt% Alumina at 532nm and 1064nm for different

Conclusion

The band gap is affected by changing the weight ratio of the Alumina filler also it is moved to red shift with increasing the weight ratio of filler. The optimum weight ratio that related to maximum nonlinear refractive index coefficient is 3% of Al_2O_3.The nanoalumina decreased the spent of energy. The nonlinear refractive index coefficient is greater at 532nm than at 1064nm and vice versa for nonlinear absorption coefficient. Different types of absorption transition were obtained ;(1PA one photon absorption, TPA two photon absorbtion and three photon absorption). It is possible to control the nonlinear coefficient for real applications by regulating the weight ratio of Al_2O_3 nanoparticle in epoxy neat and their nanocomposites Gaussian beam, the beam intensity is too weak to extract nonlinear effects.

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الخصائص ألبصرية اللاخطية للمتراكبات النانوية ايبوكسي/ألومينا

احمد حسين وهيب   زينب فاضل مهدي   رواء احمد فارس

معهد الليزر للدراسات العليا ، جامعة بغداد، بغداد، العراق

الخلاصة :درست الخواص البصرية الخطية واللاخطية للمتراكبات النانوية (الأيبوكسي/الألومينا) لمختلف النسب ألوزنية (5,3,1.5,0.5,0) % .تم الحصول على حزمة الطاقة لهذه المركبات عند هذه النسب الوزنية. أنجزت التجارب للخواص اللاخطية بأستخدام منظومة المسح على المحور الثالث الذي يحوي ليزر النديميوم – ياك ذو مفتاح عامل النوعية. أجريت التجارب لعدة عوامل : الطول الموجي (1064,532) نانومتر، وبشدة ليزر بمقدار (0,530 ، 0,679 ، 0,772) كيكا واط / سم 2والنسبة الوزنية. -النتائج اظهرت بأن حزمات الطاقة انخفضت بزيادة النسب الوزنية للالومينا ماعدا عند 5% ومعامل الانكسار اللاخطي يتناسب طرديا مع الشدات الساقطة . بينما الحالة معكوسة في معامل الامتصاص اللاخطي . تم الحصول على عدة انواع من معاملات الامتصاص اللاخطي: ظهر امتصاص فوتون وفوتونين وثلاث فوتونات أعتمادا على حزم الطاقة وطاقة فوتون الليزر. من كل ماتقدم فأن نظام المتراكبات النانوية ايبوكسي/الومينا أظهر أنه يمكن ان يستخدم كجهاز لاخطي واعد.