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Studying of Nonlinear Optical Properties of Binary Bi₂S₃ and Bi₂Te₃/PMMA Nanocomposite Films by Z-Scan Technique

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Abstract. For measuring the nonlinear refraction index n_2 and absorption index β , we have used modified Z-scan technique with the single laser beam. The media is a nanocomposite films made from the binary (Bi₂S₃ and Bi₂Te₃) with PMMA. The material is prepared via the microwave-assisted chemical method. The Characterization of the nanocomposite films was carried out using X-ray diffraction (XRD), and U-V spectroscopy. The band gaps of Bi₂S₃ and Bi₂Te₃ are 2.6eV and 2.38eV respectively. XRD shows that Bi₂S₃ and Bi₂Te₃ have orthorhombic and trigonal (hexagonal axes) structures respectively. The optical non-linearity is intensity dependent. The nanocomposite films exhibit self-defocusing nonlinearity beneath the empirical conditions. Both samples exhibit a large negative nonlinear refractive index and good nonlinear absorption coefficient with increasing laser input power. The spotted nonlinear refraction and absorption are related to thermal in nature and reverse Saturable absorption, respectively. The obtained results indicate that the nanocomposite films may open several new possibilities of using these materials in all-optical element devices.

1. Introduction

All-optical devices, which mean the effect of photons on the medium (material), cause a variation in the nonlinear properties of the material such as refraction index, absorption index, etc. The media can be any kind of materials, for example, semiconductors, polymers, or mixed of semiconductors and polymers, etc. The mixed type which is also called nanocomposite in case of one of partners in nanoscale regime. The benefits of used nanocomposite are we can tuning properties of the nanocomposite depended on properties of both portions and also properties of nanoscale materials. The nonlinear effects occur for light energy near or above than the band gap of the nonlinear material [1, 2]. The optical nonlinearities aspect in the nonlinear optical materials can be employed in many applications such as all-optical switching [3,4] and all-optical limiting [5]. The all-optical limiting is a device which displays the linear transmittance below the threshold and clamps the output to a constant above it, thus supplying safety to the eyes and sensors. The optical nonlinearity phenomenon of the nonlinear optical material can be used to realize β and n_2 were also determined using a modified Z-scan technique [6-8]. The z-scan technique is a quick, simple, and efficient method to measure the optical nonlinearities of materials.

Bismuth sulphide and telluride are a compound of tellurium and sulphur with bismuth and Poly (methyl methacrylate) (PMMA), is a transparent thermoplastic, has many properties, as a lightweight, mechanically good or resistant alternative to glass. The properties of nanomaterials depend not only on their chemical composition, but also on their structure shape, and size compares them with bulk materials. The integrated



of the semiconductor into a polymer matrix gives many advantages such as, easy processing and structural flexibility of polymers, with the optical properties and stability provided by the inorganic material [9].

The aim of this study is investigated of the all-optical limiting and nonlinear optical properties of the Bi₂S₃/PMMA and Bi₂Te₃ / PMMA under a wavelength of 532 nm CW laser by using modified Z-scan technique. The crystal structures and optical properties are characterized by using the x-ray diffraction and UV-VIS spectrophotometer techniques also.

2. Experimental details

2.1 Materials

Bismuth Chloride with the chemical formula (*BiCl*₃, sigma Aldrich) is used as is a source of bismuth, Thiourea (*S*₄*N*₄*CH*) is a source of Sulfide and Ethylene glycol (*CH*₂*OH*)₂ is solvent and Telluride powder (*Te*, Fluka) is a black powder metal. The chloroform with formula [*CHCl*₃, Scharlau] is solvent used as a homogenizer for the polymer and binary material to form films.

2.2 Preparation of samples

Binary Bi₂S₃ and Bi₂Te₃ are prepared via microwave as in [10] and chemical method as in [11]. The Bi₂S₃ synthesis from bismuth chloride (0.2 g) and thiourea (0.1 g) was dissolved in (12.5 ml) ethylene glycol and mixed together in 50 ml beaker on stirred for 1 hour. The contents were exposed to microwave irradiation in a microwave oven at power 720 W- 2 min (10s on – 20s off). The Black powder resulted from this reaction was washed many times by distilled water and ethanol to remove any unreacted reactants and impurity and then dried at 60⁰C for 2 h on battery dish.

The Bi₂Te₃ is prepared by starting materials are *BiCl*₃ (0.5g) and elemental tellurium (0.25 g) were add to the solution consist of deionized water, ethylene glycol and hydrazine hydrate in a volume ratio (7:3:1), respectively. Then, the solution was flowed back under stirring at 50⁰ C for 5 h. The precipitate is filtered by filter paper, and washed several times with distilled water and ethanol to remove any unreacted materials. After that the, powder is dried at 50⁰ C for 4 h.

The films are prepared [6] by dissolve (0.02g) of powder (Bi₂S₃ or Bi₂Te₃) in chloroform (5 ml) and stirred for an one hour. After that, we have added the PMMA as a granules (0.02g) to the solution with continuous stirring for an one hour more . Finally, the solution was cast on clean slides and left to 1-1.5 h to dry naturally at room temperature. The Bi₂S₃ and Bi₂Te₃ -PMMA nanocomposite films thickness were 108 μm and 102 μm .respectively,

The XRD is characterized by using PANalytical X'Pert PRO device with CuKα radiation (λ = 1.5406 Å). Optical absorption is measured by using UV-Vis spectrophotometer type (UV-1800 SHIMADZU) in the wavelength range from 300 to 900 nm.

2.3 Nonlinear optical measurement

Measurement of nonlinear optical properties of samples using a modified Z-scan technique [12], The transmitted intensity variation through a finite aperture placed in the far field as a function of the sample position (z) with respect to the focal plane can be measurement n_2 , which using by CW laser Nd: YAG 532 nm. The open-aperture part that all light transmitted through the sample is grouped by the lens to the detector, to measured β . The beam passes through the optical components such as Lens with a focal length of 5 cm leads to length of Rayleigh $Z_0 = 2.9$ mm and the half waist of beam $\omega_0 = 22.6$ μm . The sample is transit in the z -direction along the axis of a focused Gaussian beam. At the focus point, the sample is subjected to the maximum of intensity the light, which gradually decreases in any direction of the focus point. If the material contains a nonlinear refraction positive ($n_2 > 0$), the graph $T(z)$ has a valley first and then a peak or the sample with ($n_2 < 0$), the graph is exactly the opposite (first peak and then valley). The nonlinear absorption to either peak or valley. to measured all-optical limiting effect by stopping the sample at the near focus point, to avoid damage sample. Change of input power the laser using Natural density filter, where a change in the power output was spotted by using the optical power meter.

3. Results and discussion

3.1 UV-Visible Spectrophotometer

Optical absorption studies in the range of wavelength from 300 nm to 900 nm at the room temperature. The optical absorption spectra of Bi_2S_3 and Bi_2Te_3 -PMMA films of thicknesses 108 μm and 102 μm respectively are shown in Figure 1. It is observed no absorption peaks between 350nm and 900nm [7,8]. Consulting the previous studies, the band gap of Bi_2S_3 and Bi_2Te_3 can be explored by the extrapolation method based on Tauc's formula is The relationship between the absorption coefficient α and the incident photon energy can be written as [13]:

$$(\alpha hv) = q(\alpha hv - E_g)^j$$

where q is a constant, E_g is the band gap, j is a constant. direct transitions $j = 1/2$ and for indirect transitions $j = 2$. The value of α is obtained from the relation :

$$\alpha = \frac{2.303 A}{t}$$

where A is the absorbance and t is the thickness of the film. t is important to confirm that a.u. here means the absorbance unit, which is different from the arbitrary unit (a.u.). The linear extrapolation of $(\alpha hv)^2$ versus (hv) as shown in Figure 1 gives the value of the band gap of Bi_2S_3 and Bi_2Te_3 have 2.3 eV and 2.46 eV, respectively.

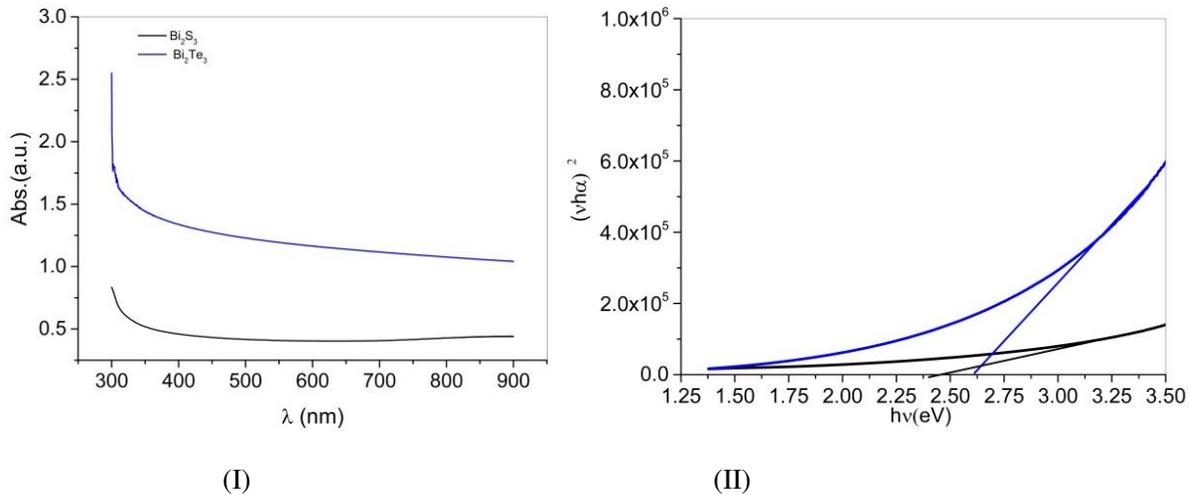


Figure 1. (I) Optical absorption spectrometer and (II) energy of Bi₂S₃-PMMA and Bi₂Te₃ -PMMA.

3.2 Crystalline structure

Figure 2. displays the XRD patterns of the powders Bi₂S₃ and Bi₂Te₃ at room temperature. The XRD patterns matched well with the standard pattern of Bi₂S₃ and Bi₂Te₃ are (JCPDS 170320 card) and (JCPDS File No. 15- 0863 from ASTM), respectively. The XRD pattern is confirmed that the crystal structure for the Bi₂S₃ and the Bi₂Te₃ are respectively the orthorhombic and the trigonal (hexagonal axes) structures. The lattice constants are calculated by using the interplane spacing equation as displayed in Table 1. The crystallite size is measured by using the Scherrer's formula :

$$D = \frac{L\lambda}{R \cos(\theta)}$$

where $L=0.9$ is the shape factor, $\lambda = 1.5418 \text{ \AA}$ is the wavelength of X-ray radiation, R the half-width of the peak and θ the diffraction angle in radians.

Table 1. The variables were calculated from X-ray

Lattice parameter's	Bi ₂ S ₃ (orthorhombic)	Bi ₂ Te ₃ (trigonal)
a	11.226 Å ⁰	4.507 Å ⁰
b	4.038 Å ⁰	---
c	10.9 Å ⁰	29.759 Å ⁰
D	13.982497 nm	11.0530266 nm
V	49.4 nm ³	52.35 nm ³

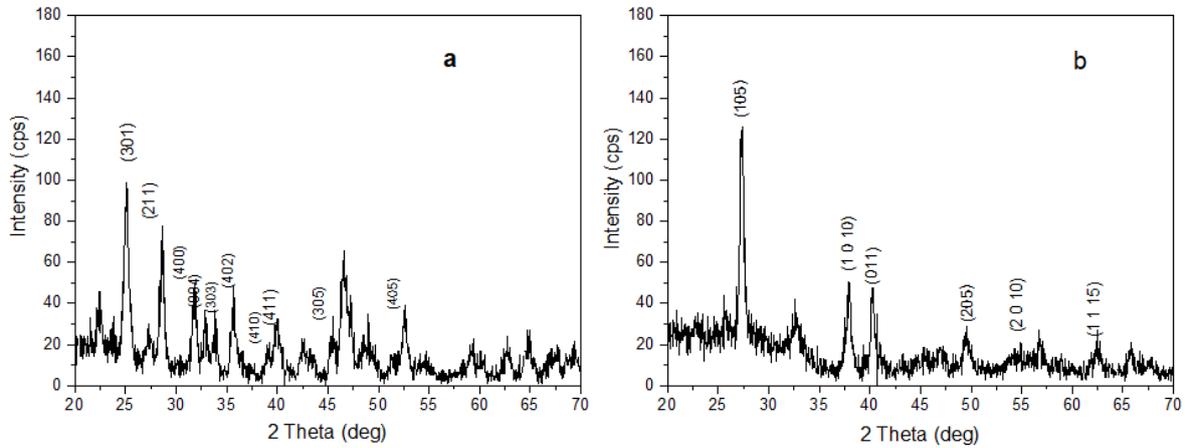


Figure 2: XRD patterns of (a) Bi_2S_3 and (b) Bi_2Te_3 .

3.3 Optical nonlinearity

In this study the effect of nonlinear optical (NLO) materials responses for Bi_2S_3 and Bi_2Te_3 -PMMA the samples transmission as a function of the sample position (z) of Z-scan sequences at different powers input. Z-scan results supplied information around the nonlinear optical parameter n_2 and β . This results of Bi_2S_3 and Bi_2Te_3 -PMMA nanocomposites were obtained laser 532 nm exhibit a good response to Interference between the material and the laser as shown in Figure 3.

The physical phenomenon cause of nonlinear refraction is attributed to thermal contribution [14]. The nonlinear refractive index is calculated from the valley to peak difference of the normalized transmittance [15]:

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

The linear transmittance of the aperture S is given by $= 1 - \exp(-r_a^2/w_a^2)$, where w_a is the radius spot of a laser beam in front of the aperture, r_a is the radius of aperture and $\Delta\phi_0$ is the phase shift given by equation [16]:

$$|\Delta\phi_0| = kL_{eff}n_2I_0 \quad (2)$$

where ΔT_{p-v} is the valley – peak transmittance difference from the closed aperture Z-scan curve. L_{eff} is the thickness effective of the sample given by $L_{eff} = (1 - \exp(-\alpha L))/\alpha$, k is the wave vector, I_0 is the intensity of the laser beam at focus and α is the linear adsorption. To measure the magnitude of the nonlinear absorption coefficient β is given by formula[16]:

$$\beta = \frac{2\sqrt{2}\Delta T}{L_{eff}I_0} \quad (3)$$

Where ΔT is the normalized transmittance given by

$$T(z) = 1 - \frac{4x}{[(x^2+9)(x^2+1)]} \Delta\phi_0 \quad (4)$$

where $x = Z/Z_0$. the parameters n_2 and β can calculate using equations (1) and (2) for the Bi_2S_3 and Bi_2Te_3 -PMMA nanocomposite and powers input are listed in Table 2.

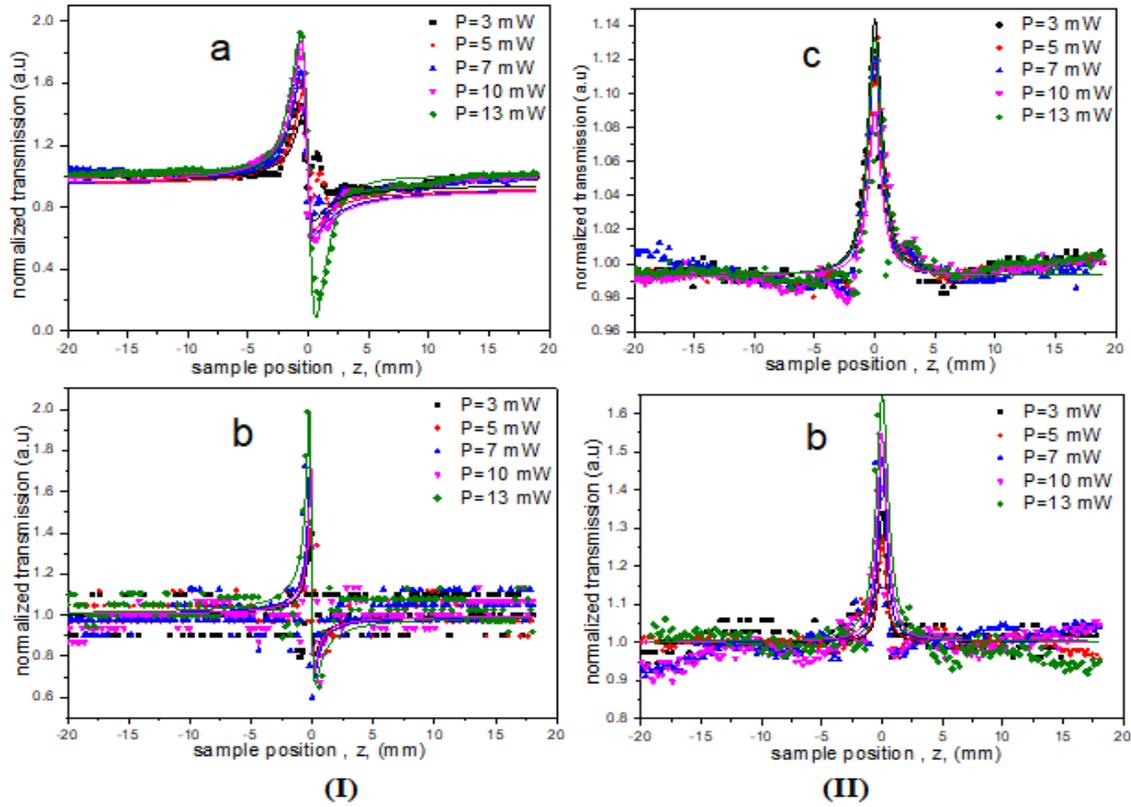


Figure 3: (I) Closed-aperture z-scans (II) Open-aperture Z-scan result at a different power input of the (a, c) Bi_2S_3 -PMMA (b, d) Bi_2Te_3 -PMMA casting nanocomposite films. The theoretical fitting is referred to as solid lines.

Table 2. Variation of nonlinear refractive index n_2 and nonlinear absorption β at different power.

material	Power (mW)	$n_2 \times 10^{-6}$ (m^2/W)	β (m/W)	W	T	F
Bi_2S_3	3	2.09561	0.06164	1.10035	1.56471	0.6391
	5	1.77379	0.03962	0.93137	1.18838	0.84148
	7	1.74813	0.02453	0.91789	0.74647	1.33965
	10	1.47067	0.01981	0.77221	0.71666	1.39536
	13	1.399	0.01016	0.73457	0.38635	2.58835
Bi_2Te_3	3	6.1799	0.03742	5.04743	0.32215	0.68975
	5	4.2532	0.01453	3.36495	0.18172	0.47471
	7	3.66122	0.01226	2.80413	0.17821	0.40863
	10	3.10814	0.01123	2.59849	0.19216	0.3469
	13	2.93616	0.01219	2.08512	0.2209	0.32771

It was observed that when the input energy gradually increased, there was a decrease in the nonlinear absorption values in Table 2 and also in nonlinear refractive values. There is a proactive step to achieve all-optical switching devices by applying the terms of Figures of Merit (W, M, F) can be calculated from the following relationships [17,18]:

$$W = \frac{|n_2|I_{mix}}{\alpha_0\lambda} > 1, \quad T = \frac{\beta\lambda}{|n_2|} < 1, \quad F = \frac{n_2}{\beta\lambda} > 2.$$

I_{mix} is that maximum permitted value of the laser intensity.

3.4 Optical Limiting measurement

One application is interesting these materials is the optical limiting in an intensity CW laser. Optical limiting is a nonlinear optical procedure in which the transmission remains constant when the transmitted intensity of the material increases the threshold region. Optical limiting could engender from self-diffraction (SD), revers saturation absorption(RSA) and thermal defocusing. Mechanism measured the optical limiting by stop the sample near focus position at peak or valley, to eschew damage sample because of high intensity in this point. The transmitted power measures through laser incident different powers show in Figure 4. The output power increases with an increase in input power this call the damaged region. At a certain threshold value, the defocusing effect occurs, which results in a greater cross-section area and Increasing the proportional with the intensity of the beam.

The first input power is very low and starts to increase gradually to reach a stable state after that value of powers increases again high. To calculate the dynamic range (DR):

$$DR = \frac{P_d}{P_{th}}$$

Table 3 listed the values of (P_{th} , P_{th} , DR) for Bi_2S_3 and Bi_2Te_3 -PMMA .

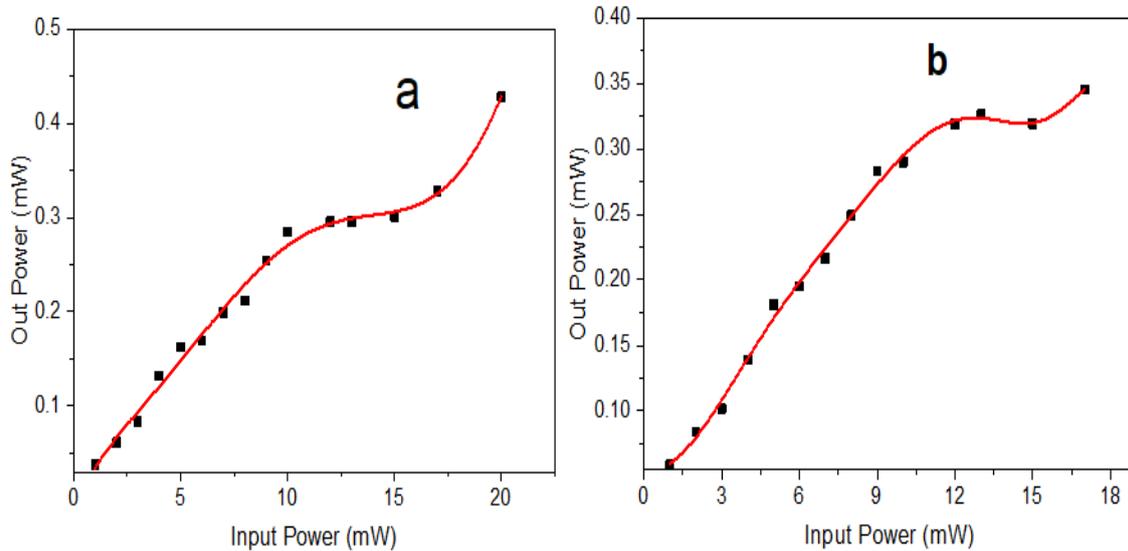


Figure 4: All-optical limiting performances (a) Bi_2S_3 -PMMA (b) Bi_2Te_3 -PMMA

Table 3. All-optical limiting parameters for Bi_2S_3 and Bi_2Te_3 -PMMA

material	P_{th}	P_d	Dynamic range, DR
Bi_2S_3	5.79	16.33	2.82
Bi_2Te_3	6.86	15.36	2.24

From the values listed in Tables 3, we deduced that the optical limiting threshold value is small and optical damage is high which are indicated that the optical nonlinearity of the films are high. The results obtained for films Bi_2S_3 and Bi_2Te_3 -PMMA has a relatively high limiting threshold and a small stability area. Optical nonlinearity mechanisms that occasion optical limiting have different types, such as self-focusing, self-defocusing, free carrier absorption, reverse saturable absorption, multiphoton absorption and two-photon absorption [15].

4. Conclusions:

The prepared films have a good mechanical quality as appeared from free-standing hanging without cracked or teared up. The mixing of the PMMA polymer is played a critical role to enhance the mechanical properties and its solution casting. The optical band gap of the films are large when compared with the optical band gap of Bi_2S_3 and Bi_2Te_3 . From the values of the third-order nonlinear susceptibility, we concluded that the nanocomposite films maybe candidate as a good materials in all-optical element devices.

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