Cu_2SnS_3 (CTS) Nanoparticle Production with Laser Ablation Method and Nonlinear Optical Properties

Hamdi Şükür KILIÇ, Yasemin GÜNDOĞDU, Amina HOUIMI and Serap YİĞİT GEZGİN

Abstract—In this study, Cu_2SnS_3 (CTS) target have been synthesized using ball milling technique with Copper (Cu), Tin (Sn) and Sulphur (S) powders. After the production of CTS target, pulsed laser ablation (PLA) in liquid method was carried out for nanoparticle form of CTS. Femtosecond (fs) laser system with 800 nm wavelengths, 90 fs pulse duration at 1kHz repetition rate has been adapted to both PLA and z-scan experimental setups. Two different nanoparticle processes were applied to CTS target in PLA method using ethanol medium depending on duration of nanoparticle production. The characterization of crystal structure will put forth in detail and obtained CTS bulk material used to obtain CTS nanoparticle in liquid medium to analysis nonlinear optical properties using femtosecond z-scan method. For these structures, nonlinear absorption coefficient values were observed to be between -6.227 x 10^{-11} cm/W and -9.946 x 10^{-11} cm/W, while nonlinear refraction indexes were measured to be from 1.331 x 10^{-16} cm^2/W to 7.328 x 10^{-16} cm^2/W. In addition, third order nonlinear optical susceptibilities for these NPs were calculated to be between 5.486 x 10^{-14} (esu) and 8.994 x 10^{-14} (esu). All obtained results will be present in detail.

Keywords— CTS, Nanoparticle, nonlinear optic, z-scan, femtosecond laser

I. Introduction

Chemical and physical structure and properties of Cu_2SnS_3 (CTS) bulk material and nanoparticle (NP) forms are affirmative enough to make them applicable in a variety of applications such as optics, photonics and electronics including solar cells, photodiodes, transistorss etc..

World energy consumption as well as demand are significantly increasing depending on the increasing population according to this situation, the need for new materials including nontoxic, earth abundant, structural extensibility, environmentally safety, simple fabrication methods elements are increasing day by day [1]. Using NP production techniques, especially that are environmentally more friendly rather than chemical production techniques, will contribute positively in today's world where global warming is common [2].

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In the literature, promising candidate as a high absorber material CTS is a direct-bandgap p-type semiconductor which has 0.8–1.7 eV optimal energy band gap range with >10^4 cm^{-1} absorption coefficient [3-5]. Cu-Sn-S is ternary structures belonging to I, IV and VI groups of semiconductors, respectively [6]. These are a number of well known materials with high absorption coefficients and low photon energy band gaps, because of these properties of such special materials, these materials have key importance for especially optoelectronic devices [7]. These elements are very capable candidate for nonlinear optical materials. Cu_2SnS_3 (CTS) is a good phase ternary compound obtained from Cu, Sn and S elements. While photovoltaic (PV) technology is developing rapidly [8], the use of CTS is therefore widely used material in this area. However, opening new areas for these kind of novel and advanced materils such as lasing [9], waveguide and other nonlinear devices will further expand the area of use as well as develop some new technologies [10]. With this motivation, in this study, firstly CTS bulk material have been produced in our laboratory using cost effective and nontoxic materials including Cu, Sn and S.

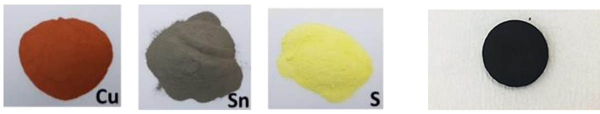
Femtosecond (fs) laser z-scan technique is the best method to determine of nonlinear optical properties [11, 12]. Investigation of the nonlinear optical properties of the CTS gives nonlinear absorption coefficient, nonlinear refractive index as well as third order nonlinear susceptibilities contributed to well-known composition, morphological, electronical, optical and surface properties, these results is very important for the spread of CTS in different applications. Using NP form of materials give different, promising approaches to various aspects of technology including lasing, optical limiting, optical data storage, computing and optical communications apparatus [13].

In this study, there are three significant step including production of target, converting it to NP form of CTS [14] and analysing its nonlinear optical characteristics. In the first step CTS target was produced in our laboratory and secondly linear and nonlinear optical characterizations carried out on CTS and details are given in details.

II. Materials and Method

A. CTS Production process

Copper (Cu), Tin (Sn) and Sulphur (S) powders (2:1:3 rate) shown in Figure 1a, steel balls (100 g balls:10 g CTS powder rate) and some acetones were added in a steel container. This wet powder mixture was mixed by a ball milling device for 6 hours and then dried in a quart tube under Argon (Ar) gas flow for 24 hours. This powder mixture was put into a special designed mold and pressed by a hydraulic press device at 30 bar pressures.



(a) **(b)**

Fig. 1. Photographs of a) Cu, Sn and S powders and b) Cu2SnS3 target pellet

Cu_2SnS_3 target pellets were annealed at 600 °C for 2 hours by placing 100 mg of Sulphur powder next to them and giving Ar gas in a quartz tube. The image of Cu_2SnS_3 target pellet is shown in Figure 1b.

B. CTS Pellet Laser Ablation In Liquid

The laser ablation experiments performed using the fundamental wavelength 800 nm operated at 1 kHz with 90 fs pulse duration Ti:Saphire laser system (Quantronix, NY). The first, the laser beam was focused by an 11 cm focal length lens designed in a micromachining unit (Quantronix, Q-Mark, NY) shown in figure 2.

Fig. 2. CTS nanoparticle production in ethanol medium using Q-Mark micromachining unit

The CTS pellet was placed in ethanol medium in a glass beaker. In ablation processes, the solutions obtained of CTS NPs were light grey in color particularly for in 10 minutes marked as CTS-10 and dark grey in 20 minutes marked as CTS-20 in table 1. The laser intensity for the output laser beam at the focal point was calculated to be 2.37 x 10^{11} W/cm^2.

C. Z-scan Experimental Setup

The investigation of the nonlinear optical characteristics of CTS in ethanol medium was performed at a wavelength of 800nm from fs laser system using z-scan technique. The Cu, Sn, S containing CTS NPs have been placed in a 2mm thick quartz cell. The samples on z-axis were moved along through the focal plane of 50 cm focal length lens using a computer controlled z-stage shown in figure 3.

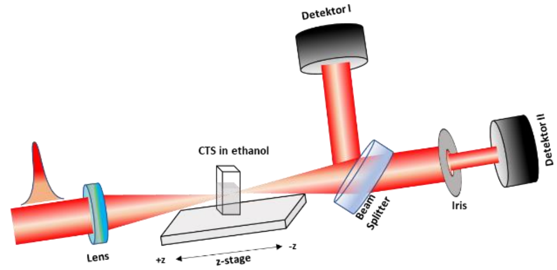


Fig. 3. Z-scan experimental mechanism used in CTS nanoparticle

III. Results and Discussion

A. Linear Optical Responses with Uv-Vis Spectroscopy

In this study, Linear optical process investigated using UV-Vis spectroscopy to determine the optical properties of the CTS NPs. The spectra shown in Figure 4 revealed that the CTS-10 and CTS-20 NPs as samples. The absorption intensity in UV region is higher than that in the infrared region for CTS NPs. The CTS NPs prepared samples were characterized using Uv-Vis spectrophotometer to obtain absorbance spectra and calculate a band gap of NPs. Band gap values of nanoparticles (NPs) to be accessed by the photon energy are calculated using Tauc curve in equation 1,

$$(\alpha h\nu)^2 = A(h\nu - E_g)^{1/2} \qquad (1)$$

where E_g is energy band gap of NPs, A and hv are area and photon energy which are constant during the experimenting, Eg is determined by straight line of $(\alpha hv)^2$ versus (hv) in Tauc plot in figure 4. The energy band gap was calculated from equation (1), which is equal to 3.4 eV and 3.7 eV for CTS-10 and CTS-20, respectively.

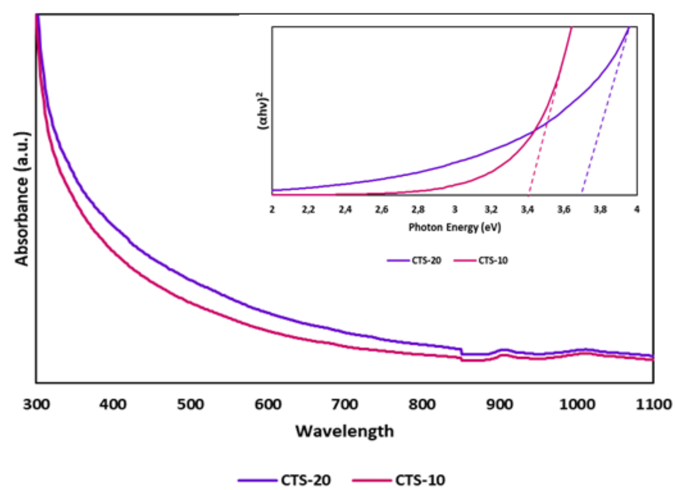


Fig. 4. UV-Vis absorption spectrum of CTS-10 and CTS-20 NPs in ethanol medium

https://doi.org/10.17758/EIRAI10.F1021117

B. Nonlinear Optical Responses with Z-scan

The nonlinear optical characterization of the CTS in ethanol medium were carried out using fs laser-based z-scan technique firstly proposed by Sheik Bahae et al [15]. The sample position dependence of laser intensity gives different beam signals due to the response of samples to the detectors therefore, the open aperture and closed aperture experiemantal data of the sample can be defined by theoretically computing z-scan curves. Obtained data from experimental curveswere fitted to equation (2) and equation (3), respectively.

$$T_{open}(x) = (\beta I_0 L_{eff} / 2.83)(1/x^2) \qquad (2)$$

The describing the relative coordinate x=z/z0, z0 is defined as the Rayleigh length, the normalized transmittance T_{closed} (x) in this instance closed-aperture z-scan can be given as:

$$T_{closed}(x) = 1+ (4\Delta\Phi_0 x / (x^2+9)(x^2+1)) \qquad (3)$$

Effective optical path length L_{eff} is equal to $(1- e^{-\alpha L}) / \alpha$ [16] and closed aperture z-scan data was fitted to equation(3). $\Delta\Phi_0$ was also calculated by using equation

$$\Delta\Phi_0=2\pi / \lambda(n_2 I_0 L_{eff}) \qquad (4)$$

In these equations, ω_0 is define as the beam waist at the focal point, λ is always wavelength of the incident beam, I_0 is symbolized as laser intensity and the absorption coefficient shown as α [16]. Open and closed aperture z-scan data for CTS-10 and CTS-20 NPs have been fitted using experimental data shown in figure 5 and figure 6, respectively.

TABLE I. MEASURED β AND n_2 NONLINEAR OPTICAL VALUES WITH LASER BEAM INTENSITY OF 2.37 X10^{11} (W/CM^2).

Sample	β (x 10^{-10} cm/W)	n_2(x 10^{-16} cm^2/W)
CTS-10	-1.402	-4.018
CTS-20	-0.806	-0.592

Fitted data for open and closed aperture experiments are exhibited in table 1 as nonlinear absorption coefficients were observed to be between -0.806 x 10^{-10} cm/W and -1.402 x 10^{-10} cm/W for CTS-20 and CTS-10 NPs, respectively, while nonlinear refraction indexes were measured to be varying from -0.592 x 10^{-16} cm^2/W to -4.018 x 10^{-16} cm^2/W for CTS-20 and CTS-10 NPs, respectively.

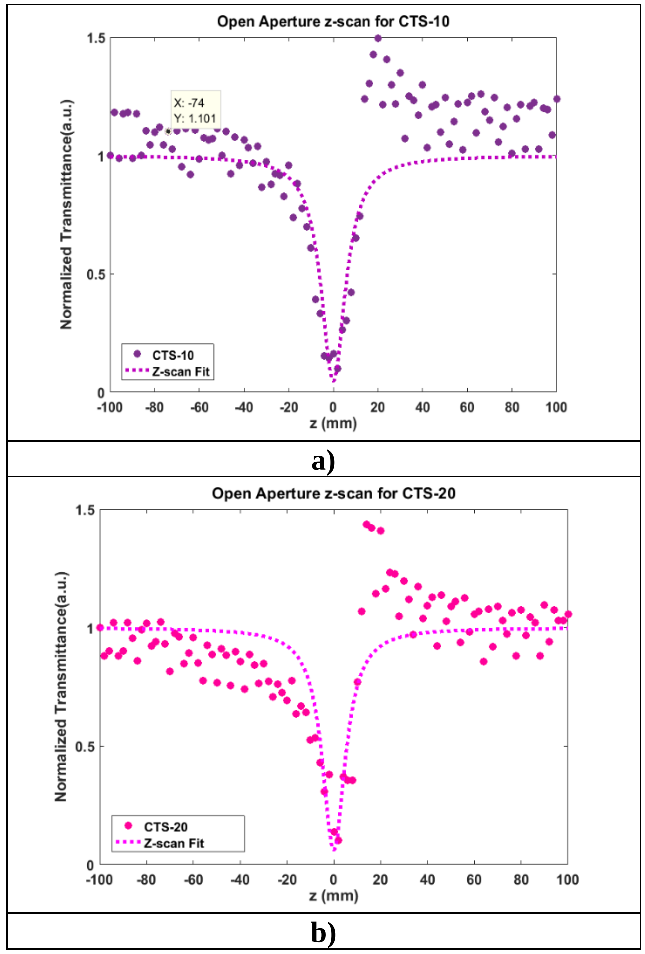


Fig. 5. OPEN aperture z-scan data for a) CTS-10 and b) CTS-20

In this study, the first measurements have been carried out for CTS NPs. Open and closed aperture Z-scan data were fitted using MATLAB program. Z-scan curves give opportunities to calculate real and imaginary parts of third order susceptibilities for CTS NPs.

$$ReX^{(3)}(esu) = 10^{-4}\frac{\varepsilon_0 c^2 n_0{}^2}{\pi} n_2 \qquad (5)$$

$$ImX^{(3)}(esu) = 10^{-2}\frac{\varepsilon_0 c^2 n_0{}^2 \lambda}{4\pi^2} \beta \qquad (6)$$

$$|X^{(3)}| = \left[\left(Re(X^{(3)})\right)^2 + \left(Im(X^{(3)})\right)^2\right]^{1/2} \qquad (7)$$

According to equation (5) and equation (6), ε_0 is defined as vacuum permittivity, the velocity of incident light is shown as c and calculated nonlinear parameterswere used to determine third order susceptibility of CTS NPs using equation (7) [17-19].

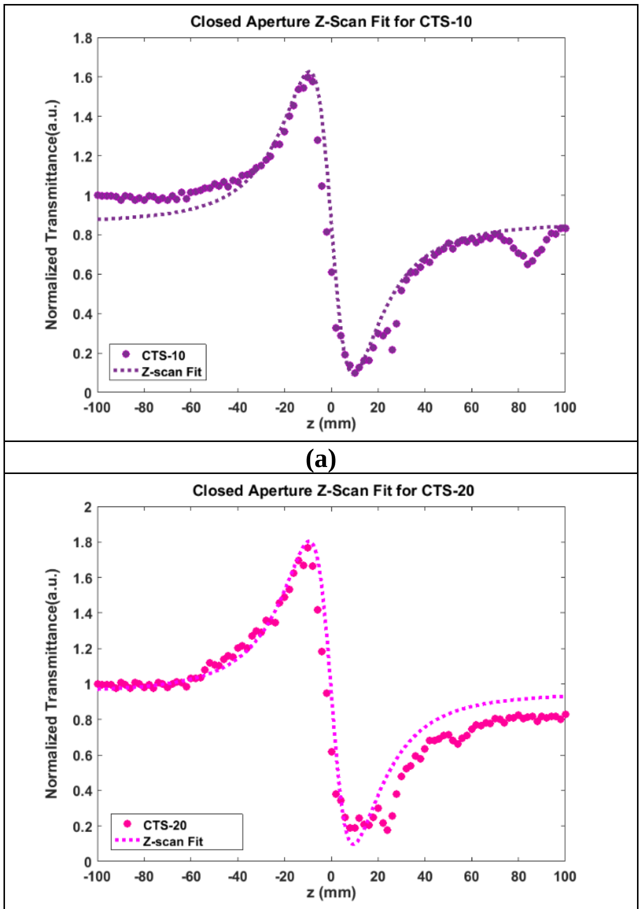


Fig. 6. Closed aperture z-scan data for a) CTS-10 and b) CTS-20

TABLE II. THE REAL AND IMAGINARY PARTS OF CTS NPS

Sample	$Re(X^{(3)})esu$	$Im(X^{(3)})esu$	$X^{(3)}$
CTS-10	-3.935×10^{-16}	-8.741×10^{-14}	8.741×10^{-14}
CTS-20	-0.476×10^{-16}	-4.124×10^{-14}	4.124×10^{-14}

Real and imaginary parts for CTS-10 and CTS-20 NPs are indicated in table 2.

IV. CONCLUSION

As a conclusion, firstly CTS pellet was produced, NP was produced using a PLA technique in liquid (ethanol) with CTS pellet. The experimental process of optical nonlinearity on CTS NPs produced by PLA which are conducted by femtosecond z-scan method. Open aperture results show saturable absorption trend in 2.37×10^{11} W/cm^2. It was found that these results show strong nonlinear optical properties at near infrared region. For these structures, nonlinear absorption coefficients were observed between -0.806×10^{-10} cm/W and -1.402×10^{-10} cm/W for CTS-20 and CTS-10 NPs, respectively, while nonlinear refraction indexes were measured to be varying from -0.592×10^{-16} cm^2/W to -4.018×10^{-16} cm^2/W for CTS-20 and CTS-10 NPs, respectively. In addition, third order nonlinear optical susceptibility for CTS NPs were calculated to be 4.124×10^{-14} (esu) and 8.741×10^{-14} (esu), respectively.

Z-scan method serves as a promising method to study the nonlinearities in NPs depends on applications. An understanding of these nonlinear optical properties provide better insight in use of CTS is therefore widely used material in this area. However, opening new areas of use such as lasing, waveguide and other nonlinear devices will further expand the area of use in technology.

ACKNOWLEDGMENT

Authors kindly would like to thank
- Selcuk University Scientific Research Project (BAP) Coordination for the support with the number 13301022 project,
- Selçuk University, High Technology Research and Application Center (İL-TEK) and SULTAN Center for infrastructures.

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