Optical Materials 85 (2018) 48–54

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Z-scan measurements of the third-order optical nonlinearities and linear optical properties of $70TeO_2$ - $5M_xO_y$ - $10P_2O_5$ - $10ZnO$ - $5PbF_2$ glasses doped with Er^{3+} ions modified by transition metals

R. Miedzinski[a,*], I. Fuks-Janczarek[a], M. Reben[b], Y. El Sayed Said[c]

[a] Faculty of Mathematics and Natural Science, J. Dlugosz University in Czestochowa, Al. Armii Krajowej 13/15, Czestochowa, Poland
[b] Faculty of Materials Science and Ceramics, AGH - University of Science and Technology, al. Mickiewicza 30, Cracow, 30-059, Poland
[c] Physics Department, Faculty of Science, King Khalid University, P. O. Box 9004, Abha, Saudi Arabia

ARTICLE INFO

Keywords:
Optical materials
Glasses
Z-scan method
Two-photon absorption
Rare earth ions
Energy gap

ABSTRACT

The two photon absorption (TPA) coefficient (β), the nonlinear refractive index (n_2), and the third order nonlinear optical susceptibility ($\chi^{<3>}$) of tellurium dioxide glasses were investigated using the absorption spectra, normalized transmission, and Z-scan methods. We studied the influence of different transition metals, with and without the rare earth ion Er^{3+}, on the nonlinear properties of these glasses. The experimental results show that (n_2) and (β) are the highest for the glass consisting of cadmium oxide doped with rare earth ions. Consequently, the real and imaginary part of the third-order nonlinear optical susceptibility ($\chi^{<3>}$) is the highest for these materials. Moreover, the presence of Er^{3+} increased the NLO coefficients the all the examined samples. The Z-scan result confirms, the glasses exhibit self-focusing effects and the sign of the refractive nonlinearity is positive.

1. Introduction

The study of nonlinear optical properties of materials has been pushed by the need to develop novel technologies in optics and photonics, such as all-optical switching [1,2], optical limiting [3,4], and amplifiers [5,6]. Different types of solid-state materials, from polymers to crystals [7–9], have been developed and investigated as feasible candidates for such purposes [10]. Aside from their mechanical stability, ease of handling, and fast production process, which makes them useful for several purposes. In this direction, they also posses excellent optical properties and the flexibility to be produced using different compositions and shapes. In recent years, particular attention has been given to tellurite glasses and researchers have found advanced applications for them. Oxyhalide tellurite glasses, co - embedded with Er^{3+}-Yb^{3+}, was successfully used in amorphous silicon solar cells [11]. In addition and it was also reported that the erbium-doped fluorotellurite glasses with different modifier oxides can effectively influence photoluminescence as well as photoinduced piezo-optical properties [12]. For the acoustically and optically operated devices, Er^{3+}-Pr^{3+} doped tellurite systems were investigated for their optical operation by sound velocities [13]. However, there are only a few reports available on the nonlinear characteristics of rare-earth-doped tellurite-based glasses. In particular, tellurite glasses exhibit:

- excellent third-order nonlinear optical properties
- high refractive index
- low cut-off phonon energy
- good transmittance
- large mechanical resistance
- high chemical durability
- high vitreous stability
- and high solubility of RE ions in doping species [14,15].

The nonlinear optical responses are comprised of two different mechanisms: nonlinear refraction and nonlinear absorption. The nonlinear absorption can be further classified into two types: saturable absorption and reverse saturable absorption. Nonlinear refraction includes the third- and higher-order nonlinear refractions as well as the cascaded second-order nonlinear refraction [16]. These optical parameters, are very important in nonlinear optical systems [17–19].

The purpose of this work is to determine the nonlinear refractive index, nonlinear absorption, and nonlinear susceptibility of $(z-5)TeO_2$ - $5M_xO_y$ - $10P_2O_5$ - $10ZnO$ - $5PbF_2$ glasses, prepared with Er^{3+} ions and different transient metals, using a nanosecond Z-scan technique. The

* Corresponding author.
E-mail addresses: r.miedzinski@ajd.czest.pl (R. Miedzinski), i.fuks@ajd.czest.pl (I. Fuks-Janczarek), manuelar@agh.edu.pl (M. Reben), omn_yousef2000@yahoo.com (Y. El Sayed Said).

https://doi.org/10.1016/j.optmat.2018.08.033
Received 4 June 2018; Received in revised form 16 July 2018; Accepted 11 August 2018
0925-3467/

Table 1
Composition of examined glasses.

Glass name	TeO_2	M_xO_y	P_2O_5	ZnO	PbF_2	Er_2O_3
	(%)	(%)	(%)	(%)	(%)	(ppm)
Nb_2O_5	70	5 Nb_2O_5	10	10	5	0
Nb_2O_5:Er_2O_3	70	5 Nb_2O_5	10	10	5	600
CdO	70	5 CdO	10	10	5	0
CdO:Er_2O_3	70	5 CdO	10	10	5	600
WO	70	5 WO_3	10	10	5	0
WO_3:Er_2O_3	70	5 WO_3	10	10	5	600

relationship among the obtained nonlinear refractive index with the linear refractive index, band gap energy, Urbach energy, nonlinear absorption and nonlinear third-order susceptibility are discussed.

2. Preparation of the materials, measurement and theory

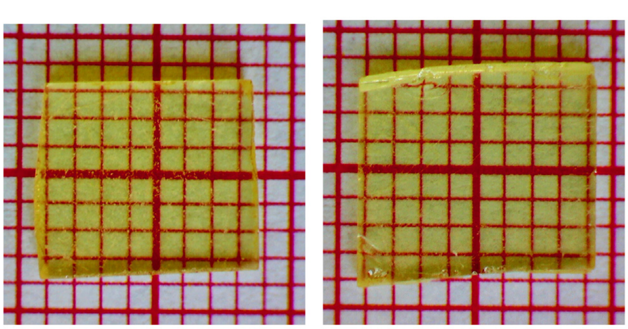
2.1. Chemical characterization

The mixture of TeO_2, Nb_2O_3, CdO, WO_3, P_2O_5, ZnO, PbF_2, ZnO, and Er_2O_3 (high purity), for 50 g batches, was homogenized in gold crucibles, melted for approximately 30 min in a preheated electrical furnace at temperatures of $T \approx 859^o$ C. While melting, the glassy alloy was stirred from time to time to improve the homogeneity. After the synthesis and homogenization, the melt was poured into a graphite mold and annealed for 2 h at 320^{o}C, then slowly cooled to an ambient temperature. The compositions of glasses $70TeO_2$ - $5M_xO_y$ - $10P_2O_5$ - 10ZnO - $5PbF_2$ in mol% where M_xO_y = (Nb_2O_3, CdO, WO_3), doped with 600 ppm Er_2O_3, are listed in Table 1.

The photographic examples of the obtained materials are showed in Fig. 1. The photograph (a) shows the $70TeO_2$-$5Nb_2O_5$-$10P_2O_5$-10ZnO-$5PbF_2$ sample, (b) shows the $70TeO_2$-$5Nb_2O_5$-$10P_2O_5$-10ZnO-$5PbF_2$ sample doped with Er^{3+}. The other four samples - containing cadmium oxide and tungsten oxide with and without rare earth ions look similar. As is shown, the obtained glasses were clear, transparent and colorless with a very yellowish tint and a thickness of about 2 mm. No crystalline inclusions were detected within a sensitivity of X-ray diffraction.

2.2. Z-scan experiment

The Z-scan technique is a simple and effective tool for us to determine the nonlinear properties. 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 the real and imaginary parts of nonlinear susceptibility, but also their signs. Both nonlinear refraction and nonlinear absorption in solid and liquid samples can be rapidly measured by the Z-scan technique, which utilizes self-focusing or self-defocusing phenomena in optical nonlinear materials [20,21]. The *Z*-scan technique, developed by Sheik-Bahae et al. [22,23], allows to estimate the basic, nonlinear optical properties of a wide group of materials. NLO parameters of crystals, glasses as well liquids, can be measured using this method. All the Z-scan measurements were carried out at room temperature. The experiment for measurement of nonlinear optical properties was performed in two parts. At first, the photo detector was kept fully open, aperture (A) was removed, which is known as a open aperture (OA) *Z*-scan. Then an aperture (A) was inserted in front of the photo detector, this is known as a closed aperture (CA) Z-scan. From the OA *Z*-scan data one can measure the nonlinear absorption coefficient β, whereas from the closed aperture *Z*-scan data the sign and magnitude of the nonlinear index n_2 can be determined. Due to its simplicity and ease of data interpretation, this technique has gained a lot of attention and has been widely accepted in the field of nonlinear society. Generally, the fraction transmitted by the aperture in the closed mode is about 40%. An experimental set-up for *Z*-scan measurement is presented in Fig. 2.



(a) (b)

Fig. 1. Photographs of the prepared samples. (a) $70TeO_2$-$5Nb_2O_5$-$10P_2O_5$-10ZnO-$5PbF_2$, (b) $70TeO_2$-$5Nb_2O_5$-$10P_2O_5$-10ZnO-$5PbF_2$ doped with 600 ppm of Er_2O_3.

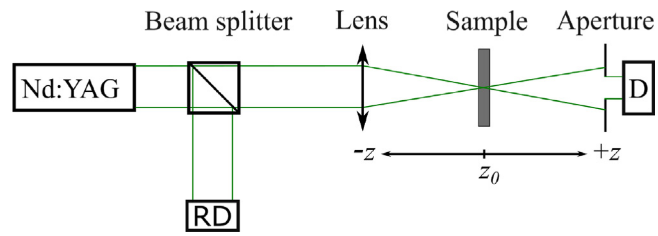


Fig. 2. Z-scan setup. RD - reference detector, D - detector of the transmitted light through the sample.

As shown, the set-up comprises of a Nd:YAG laser, delivering 2–5 ns pulses at 532 nm wavelength and other optical elements. Reference detector (RD) and (D) allow to determinate the light transmission $T(z)$ in the function of the sample (S) position in the Z axis. The output beam is focused in z_0 point by 50 mm converging lenses. At this point, the light irradiation I_0 is the highest and in our case was 5.2 (GW/cm^2). Both β and n_2 NLO coefficients are related to the third-order nonlinear electric susceptibility:

$$\chi^{(3)} = \sqrt{(\chi_R^{(3)})^2 + (\chi_I^{(3)})^2} \quad (\mathrm{m^2/V^2}) \tag{1}$$

Where the real part of third-order nonlinear optical susceptibility $\chi_R^{(3)}$ is given by:

$$\chi_R^{(3)} = 2n_2 n_0^2 \varepsilon_0 c \tag{2}$$

As shown in the eq. above, the real part of $\chi^{(3)}$ describes the nonlinear refractive index change n_2 extracted from the *Z*-scan measurements. The constant c listed in eq. (2), is the speed of light, λ is the wavelength, n_0 is the linear refractive index and ε_0 represents electric permittivity. The imaginary part of third-order nonlinear optical susceptibility is expressed as follows:

$$\chi_I^{(3)} = (\varepsilon_0 c \lambda n_0^2/3\pi)\beta \tag{3}$$

This part is related to the two photon absorption (TPA) coefficient (β) calculated from the transmission measurement. The open transmission curve estimated during the *Z*-scan experiment can be described using the following formula:

$$T(z) \approx 1 - \frac{q_0}{2\sqrt{2}} \frac{1}{\left(1 + \frac{z^2}{z_0^2}\right)} \tag{4}$$

Listed in the above equation, q_0 and Z_0 represents:

$$q_0 = \beta I_0 L_{eff} \tag{5}$$