Optical non-linearity in ZnO doped TeO_2 glasses

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In the present work we investigate the optical non-linearity and the optical limiting behaviour of TeO_2-ZnO glasses with mole fraction of 0.20, 0.25 and 0.30 ZnO content. The measurements on these glasses, prepared by conventional melting procedure, were carried out using a single beam Z-scan technique. The effective nonlinear absorption coefficients were evaluated and the nonlinear transmission of the glasses were studied as a function of the input fluence. We could observe that these materials exhibit reverse saturable absorption which makes them potential candidates as optical limiters. The band edge is seen to shift to lower energies with increasing ZnO content thus enhancing the two photon absorption which results in a decrease in optical limiting threshold.

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1. Introduction

Tellurite glasses are finding widespread applications in the field of Photonics. like chalcogenide glasses, due to some of its characteristic features like high refractive index, low phonon energy, low transition temperature and excellent infrared transmission [1-5]. It has been reported that, these glasses are good candidates for hosting rare-earth ions because of their low phonon-energy environment, good chemical durability and optical properties [6-9]. These would find application in pressure sensors or as a new laser host. The erbium-doped tellurite glasses also have shown optical and chemical properties suitable for photonic applications such as laser light modulators, optical limiters and are thermally stable for fiber drawing [10].

Studies on TeO_2–ZnO glass system have been focused on the glass formation and structural properties. The TeO_2-ZnO system is having good and stable glass-forming ability with a broad region. The glass formation depends on the cooling rate and the size of the melt, and in the TeO_2-rich region [1]. It is evident from the literature, that these glasses possess two types of basic structural units, namely TeO_4 trigonal bipyramids (tbp) and TeO_3 trigonal pyramid (tp) depending on the content and type of the modifier being used [11]. Zinc Tellurite glasses are well known for their high refractive index values. It has also been reported that glasses with a high density along with a low dispersion usually have a high non-linear refractive index. Many heavy metal oxide glasses are reported to have a high density (refractive index) and excellent non-linear properties [11]. There is a major interest in making optoelectronic and signal processing devices for communication purposes and computing applications [12,17]. Optical glasses are reported to be promising candidates for optoelectronic devices because they can be made to possess a rapid non-linear response to an optical signal. However, not much research on the non linear optical properties of zinc tellurite glass has been reported in the literature. The aim of this paper is to present one of the latest developments in non linear properties of TeO_2-ZnO glass system. The nonlinear characterization includes the laser intensity dependant non linear absorption studies of these glasses which is highly significant in areas such as passive optical limiting and optical switching [13].

2. Experimental

Glass samples for the present work were synthesized by rapid melting quenching method. The samples consists of $TeO_{2(1-x)}$– ZnO_x with x = 0.2,0.25,0.30.The zinc tellurite glasses were prepared from commercial powders by mixing the required weights of batches using tellurium (IV) oxide (TeO_2 Technical grade, Alfa Aesar) and zinc oxide (ZnO,99.99%, Assay, Alfa Aesar). The glass starting materials were weighed using electronic balance after batch calculation. The glass batch was melted in a platinum crucible at 800 ◦C and cast into a pre-heated rectangular brass mold at 280 ◦C in an air atmosphere. All the melting processes were done using an electric furnace manufactured by High heat furnace and refractories. Each glass sample was immediately transferred to an annealing furnace at 350 °C and slowly cooled to room temperature [6].These samples were then polished using various grades of silicon carbide powder for obtaining parallel, smooth and clear surface for experiment. The thickness of the glass specimens was measured using a digital micrometer gauge. X-ray diffraction technique was employed to verify their amorphous nature.

The optical absorption spectra of the glass samples where determined using JASCO V-570 double beam UV-visible spectrophotometer. The indirect band gap of the glass is estimated from the graph of hν *Vs* $(\alpha h\nu)^{1/2}$.Refractive indices were determined from the band gap [8,9] as well as Brewsters angle measurement.

In this investigation, we have used the single-beam z-scan technique [18] with nanosecond laser pulses to measure the nonlinear optical absorption properties of $TeO_2(1\text{-}x)$– ZnO_x glasses. A Q-switched Nd: YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source for the experiment. The sample is moved in the direction of the incident light (z- direction) near the focal point of the lens with a focal length of 20cm. The radius of the beam waist ωo is calculated to be 42.56μm. The Rayleigh length, $z_{0=\pi}\,\omega o^2/\lambda$, is estimated to be 10.06 mm, [20] which is much greater than the thickness of the sample, which is an essential condition to be satisfied for z-scan experiments. The reference beam energy, transmitted beam energy, and their ratio are measured simultaneously by an energy ratio meter (Rj7620, Laser Probe Corp.), which is having two identical pyroelectric detector heads (Rjp735). At the focus the power output of the laser beam was measured in GW/cm^2. The calibration of the z-scan system is done using Carbon disulfide as a standard[19]. The effect of fluctuations in the laser power observed is eliminated by dividing the transmitted power by the power obtained at the reference detector. The experiment is repeated for five different laser powers. The data are analyzed by using the procedure described by Sheik Bahae et al[18] and the nonlinear absorption coefficients are obtained by fitting the experimental z-scan plot with the theoretical plots.

3.Results and discussion

The optical absorption spectra of TeO_2-ZnO glass samples obtained in the wavelength range of 200-800 nm is shown in Fig. 1. It is clear that there is no sharp absorption edge which corresponds to the characteristics of the glassy state. Generally, the absorption edge of these glasses is determined by the oxygen bond strength in the glass-forming network. Any change of oxygen bonding in the glass network, for instance, the formation of non bridging oxygen, changes the characteristic absorption edge. For glasses and amorphous materials **α** is given by the relation [14,15]

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^n / \hbar\omega, \qquad (1)$$

where,B is a constant and **n** is an index which takes values of 2,1/2 for indirect and direct transitions. In the case of present samples, the position of the fundamental absorption edge shifts to higher energy region with increasing TeO_2 content in the glass network. It is reported that addition of ZnO to the tellurite network causes some type of structural rearrangement of the atoms leading to the increase in density which is related to variation of the molar volume of the samples**.** The decrease in the molar volume is explained as due to the decrease in the bond length or inter-atomic spacing between the atoms which may be attributed to the increase in the stretching force constants of the bonds inside the glass network. The radius of Zn^{2+} (0.074 nm) is much smaller than that of Te^{2+}(0.097 nm) [1,16] resulting in a (say brief structure) denser glass[1].

It is clear from previous works, that the tellurite glass structure will be modified by the addition of ZnO that consist of Zn^{2+} ,creating more non-bridging oxygen (NBOs) in the tellurite glass network[16]. ZnO will break up the continuous network and the divalent cation Zn^{2+} will then produce two new non-bridging oxygen ions each. The degree of crosslinking decreases as the mole fraction of ZnO increases. As a result of the non-directed bonding to cations, the structural network collapses into a close packing and hence the density increases [16]. The NBOs produced will change the glass structure in such a way that ,packing of the molecule becomes denser as more network modifier ions, attempt to occupy the interstices within the network. An increase of the density of the glasses accompanying the addition of ZnO is probably caused by a change in crosslink density and coordination number of Te^{2+} ions[16].

The shift of the ultraviolet absorption band to longer wavelengths corresponds to transitions to the NBO which bound an excited electron less tightly than the bridging oxygen [1]. The general appearance of the optical absorption spectra of zinc tellurite glasses is similar to that reported in the literature [1].

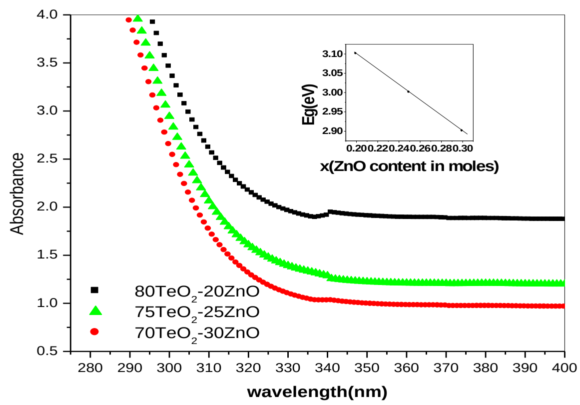

Fig.1. Absorption spectra of $TeO_2(1\text{-}x)$– ZnO_x glass(variation of band gap with ZnO content is shown in inset)

The band gap of the prepared zinc tellurite glasses is found to be within the range 2.9-3.1eV. The X-ray diffraction pattern of all the three glass samples were found without any discrete or continuous sharp peaks and exhibit broad halo at around 2Θ ≅ 26-30°, which verify the amorphous nature of the glass sample.

Measurement of optical non-linearity was carried out using a single beam z-scan technique given by Sheik Bahae *et al*. The nonlinear absorption coefficient β can be obtained from the open aperture Z-scan data by fitting the normalized transmittance data to the open aperture formula given by [18]:

$$T(Z,S=1)=\sum_{m=0}^{\infty}\sum_{m=0}^{\infty}\frac{[-q_o(z)]^m}{[m+1]^{3/2}}|q_o(z)|<1 \quad (2)$$

where $q_0(z)=\frac{[I_0\beta L_{eff}]}{1+(Z^2/Z_0^2)}$ and

$Z_0 = k\omega_0^2/2$, is the diffraction length of the beam **k = 2** π **/λ** is the wave factor , ω_o = the beam waist radius at the focal point, L_{eff} = **(1-exp(-αL))/ α** is the effective thickness of the sample.Fig.2 shows the open aperture curve of $TeO_2(1\text{-}x)$– ZnO_x system at 0.100 GW/cm2 of input laser power density. The solid curves in the figure are the theoretical fit to the experimental data.

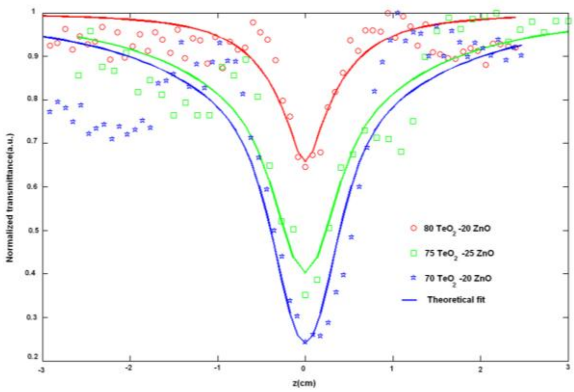

Fig. 2. Open aperture curve of TeO2(1-x)– ZnOx glass system at .100 GW/cm2 (The solid curves in figure are the theoretical fit to the experimental data).

In open aperture experiment, transmittance curve exhibited by the glass samples give an enhanced valley which is an indication of Reverse Saturable Absorption (RSA) .It is clear from the data that the material is a two photon absorber.Here it is observed that as ZnO content is increased, band gap is shifted to lower value. The band gap redshift enhances two photon absorption and results in an increase in nonlinear absorption. The non linear absorption coefficient is calculated from the fitted data. The open aperture curve of $75TeO_2$-25ZnO at three different powers are plotted in Fig. 3.. Nonlinear absorption coefficient β is found to decrease with increase in laser power , as reported earlier[22], which can be due to the removal of an appreciable fraction of photocarriers from ground state. Thus when incident intensity exceeds the saturation intensity, absorption coefficient of the medium decreases which is tabulated in Table.1.

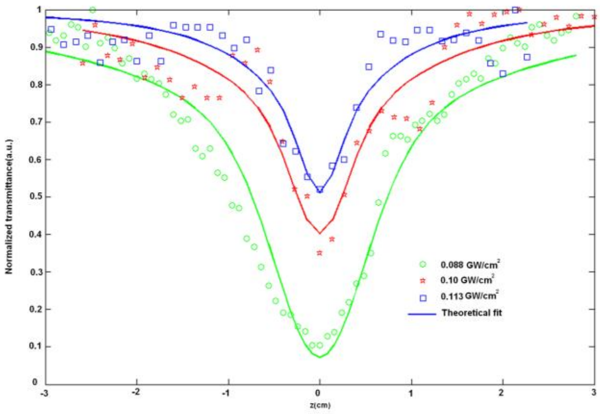

Fig. 3. open aperture curve of $80TeO_2$-20ZnO at three different powers. (The solid curves in figure are the theoretical fit to the experimental data)

One of the applications of reverse saturable absorbing materials is in devices based on optical limiters. Optical limiters are materials that allow light to pass through them at low input intensities, but become opaque at high inputs.

To check whether the zinc tellurite glasses behave as optical limiters, the nonlinear transmission of the glass is studied as a function of the input fluence. An important factor in the optical limiting behavior is the limiting threshold. The lower the optical limiting threshold, the better the optical limiting material [21].

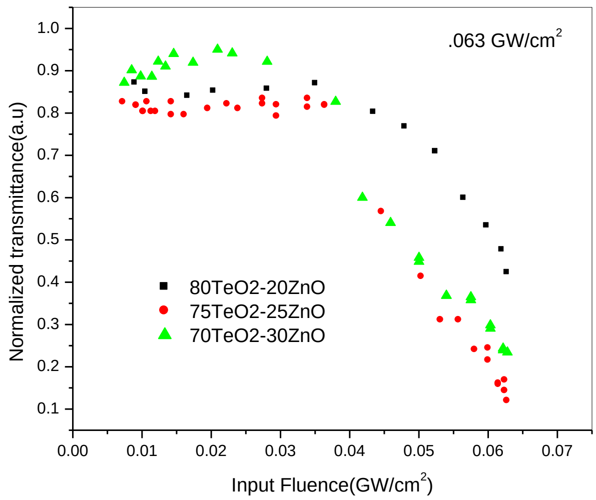

Fig. 4. Optical limiting response of $TeO_{2(1-x)}$– ZnO_x glass system at .063 GW/cm2.

The nonlinear transmission of glass samples is studied as a function of the input fluence,by generating fluence values using the equation

$$I(z) = \frac{I_0}{\left[1 + \frac{Z^2}{Z_0^2}\right]} \quad (3),$$

where I_0= the power output of the laser beam at the focus, and Z_o= diffraction length of the beam. This plot is a clear evidence to the optical limiting behavior of the glass samples. Optical limiting response of $TeO_2(1-x)$– ZnO_x glass system at .063 GW/cm^2 is shown in Fig. 4. It is found that that the optical limiting threshold of the glass increases with increase in laser power.

The obtained values of the nonlinear absorption coefficient and optical limiting threshold for various powers are shown in Table 1.

Table 1. Nonlinear absorption coefficient and optical limiting threshold for various powers

sample	Eg(eV)	Refractive index n	Input laser power density x 10^{-3} (GW cm^{-2})	β (cm/GW)	Optical limiting threshold x 10^{-3} (GW cm^{-2})
80TeO2-20ZnO	3.1	1.80	63	396	35
			75	341	41
			88	296	49
			100	198	71
			113	255	80
75TeO2-25ZnO	3	1.96	63	574	36
			75	469	38
			88	424	56
			100	325	71
			113	269	72
70TeO2-30ZnO	2.9	2.05	63	1215	21
			75	1033	23
			88	888	42
			100	754	55
			113	673	67

As given in the table it is evident that there is an increase in the optical nonlinearity with ZnO content in zinc tellurite glasses .Large value of refractive index results in larger magnitude of optical nonlinear interaction and so larger non linear absorption resulting in lowering of optical threshold.

4. Conclusions

The optical properties of zinc tellurite glasses were found to be affected by changes in glass composition . The open aperture curve exhibited by the glass sample gives an enhanced valley showing that the material exhibits reverse saturable absorption. Nonlinear absorption coefficient β is found to increase with increase in ZnO content. Also the nonlinear transmission of the glass studied as a function of the input fluence shows that Optical limiting threshold of the glass increases with increase in laser power. The refractive index of TeO_2-ZnO glasses increase with substitution of ZnO into TeO_2. The band gap red shift enhances TPA which in turn results in a decrease in optical limiting threshold.

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