

AN OVERVIEW OF NONLINEAR OPTICAL PROPERTIES OF CHALCOGENIDE GLASSES FOR OPTICAL LIMITING APPLICATIONS

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Abstract

The protection of photosensitive objects from lasers is highly required, particularly, in the field of defence. Such devices are called Optical limiters. High transmission for low inputs is essential so that the device must have low linear absorption. So, the materials showing two-photon-absorption (TPA) and third order non-linear optical properties become desired candidates for optical limiting devices. The transparency of chalcogenide glasses lies up to the mid infra-red. They show large Kerr nonlinearity and have ultrafast response time. These properties make chalcogenide glasses a suitable candidate for optical limiting. In the present work an overview of the experimental parameters required for optimized optical limiting applications have been reviewed and presented.

Keywords: Nonlinear refractive index, two photon absorption, Z-scan, optical bandgap

1. Introduction

Optical limiters find usage in protecting instruments that are sensitive to high optical radiation. They can be particularly use in defence like protecting the sensing devices from laser weapons. Many materials have been used in optical limiting (OL) like vanadium dioxide (VO_2) but due to high temperatures required for deposition and a fixed number of substrates available for deposition restricts its application in device fabrication [1]. Organic molecules are also used in OL but they are generally environmentally unstable and may get damaged at high intensities. Wide range of other materials have also been used [2-5] but, ease of synthesis and thin film deposition of chalcogenide glasses makes them a striking choice for OL devices.

Chalcogenide glasses have nonlinear refractive indices much higher than silica. Chalcogenide glasses are composition dependent which means that their properties can be tuned as per the requirement [6]. *Tellurium* based chalcogenides have been reported to have highest third order nonlinear optical properties but they are not suitable for OL due to high optical linear absorption [7]. *Selenium* based chalcogenide glasses have moderate nonlinear optical properties. Arsenic based compositions show high non linearity and have been reported extensively [8]. But arsenic is highly toxic and hazardous to work with.

Optical limiters are generally of two types: dynamic and passive. A dynamic OL consists of a photodetector, a logic circuit for comparing the measured intensity with a reference value and an

optical limiting device. A major drawback of dynamic limiters is the electronic response time of the circuit which limits its effectiveness. A passive OL relies on intrinsic properties like two photon absorption, non-linearity etc which cannot be easily altered. But the existing passive devices are often destroyed due to overheating due to intense laser irradiation. Hence, they have to be replaced periodically. A reflective type optical limiter consists of a nonlinear defect layer sandwiched between two lossless Bragg reflectors [9]. The chalcogenide layer introduces a defect mode into the Bragg reflector, allowing for the transmission of a narrow band of radiation within the photonic band gap. At low incident thresholds, the defect layer has few to no losses, the defect mode disappears, and the whole stack becomes reflective. Because no absorption occurs, the limiter is not destroyed and can be used again.

The present work summarizes some of the important chalcogenide compositions and their NLO parameters determined using Z-scan technique. The Z-scan results for open aperture and closed aperture mode have been discussed which clearly indicate at the type of mechanism taking place in the glasses. At some places a comparison between different compositions has also been made and the main focus is at finding the optimized nonlinear optical parameters for using a particular chalcogenide glass composition as optical limiter in photonic devices.

2. Experimental Results

Lu *et al* [10] reported the third order optical nonlinear (TONL) properties of $(100-x)$ $(60\text{GeS}_2-40\text{Sb}_2\text{S}_3)$. x CdCl_2 ($x = 0, 10, 20, 30, 40, 50, 60$ in mol%) glasses which were prepared using melt quench technique. The linear parameters of the chalcogenide system were determined from the optical transmission spectra. The transparent window of the glasses varied from $0.6-11\mu\text{m}$ and E_g got enlarged. The nonlinearity of the glasses has been studied using Z-scan method. In the closed-aperture (CA) peak-following-valley trace suggested positive value of n_2 which decreases with CdCl_2 concentration. However, the valley trace for open aperture (OA) implies reverse-saturated absorption (RSA). The TONL followed TPA process and the TPA coefficient (β) also decreases with the gradual increase of CdCl_2 . For $x = 60$, the figure of merit (FOM) < 1 meeting the optical switching criterion [11] making the glasses favourable photonic materials for all optical switching.

Chen *et al* [7] have explored the TONL properties of *As* and *Ge*-free chalcogenide glasses. They have investigated environmental friendly and low-cost selenium based systems within a *Ga-Sn-Se* (GSS1 – GSS7 in mol%) ternary system. The selenium percentage is decreasing in the samples by varying either *Ga* or *Sn*. The linear refractive index, assessed using infrared variable angle spectroscopy ellipsometer, varies between the range 2.56 to 2.65 and E_g almost decreases from GSS1 to GSS7 from 1.53 to 1.63 eV. The NL parameters have been characterized using $D4\sigma$ -Z-scan at $\lambda = 1.064\mu\text{m}$ in the picosecond (ps) regime. The n_2 values are found to be positive and the normalized n_2 (to silica glass) values increase for GSS1 to GSS7. The maximum value of GSS7 is 2912 times the silica glass. The n_2 values have also been compared to other *Se* based chalcogenide glasses [12-14]. The classical OA Z-scan measurements confirm the presence of a NLA phenomenon at $1.1064\mu\text{m}$. The β is also maximum for GSS7 indicating that the two-photon resonant augmentation along with TPA may be a substantial contribution to the large nonlinear refraction of the GSS chalcogenides.

Mandal *et al* [15] have employed Z-scan technique, with near $E_g = 532$ nm excitation laser, for the analysis of NLO response in $As_{50}S_{50}$ thin films. The band gap of the $As-S$ thin film, evaluated using the Tauc's equation, comes out to be 2.05 ± 0.01 eV. In the OA scheme, the nonlinear response of the thin film shows RSA similar to Elim *et al* [16]. Since the transmission values remain the same it means that thin film has not undergone any photo or thermal damage when illuminated with laser. In the CA measurements (peak intensity 30 MW cm^{-2}) peak-valley behaviour was observed which is related to self-defocusing effect and negative n_2 values. The axial peak valley difference was greater than $1.7 Z_R$ which proves the thermal contribution and third order process. The reported values of n_2 are approximately $(8.49 \pm 0.81) \text{ cm}^2 \text{ GW}^{-1}$, and $\text{FOM} \sim 0.06$. n_2 have been claimed to be seven times greater than the fused silica. The studied glasses were posed as strong candidates as optical limiters for optoelectronic devices.

Pradhan *et al* [17] discussed the TONL properties of $As_{40}Sb_7Se_{53}$ and $As_{40}Sb_{10}Se_{50}$ using 1064 nm, 5 ns pulses of Nd:YAG laser. The OA Z-scan technique has been employed. The E_g values calculated using the optical transmission spectra were reported to be 1.728 ± 0.003 eV and 1.752 ± 0.002 eV for $As_{40}Sb_{10}Se_{50}$ respectively. For $As_{40}Sb_7Se_{53}$ sample, at low intensity of 11 MW/cm^2 saturable (SA) was observed while at higher intensities of 13, 32 and 37 MW/cm^2 RSA was observed. On the other hand, for $As_{40}Sb_{10}Se_{50}$ no nonlinear optical response was noticed below threshold peak intensity of 25 MW/cm^2 and since the E_g was above photon absorption energy so, NL absorption was reported to be associated with TPA. The NL effects were explained by assuming a three-level model constituting conduction band, valance band, and chalcogenide glass defect states. Onset and optical limiting threshold intensity (F_{ON} and F_{OL}) are important parameters in deciding the performance of an OL. F_{ON} and F_{OL} should be very low for an ideal optical limiter [18]. For $As_{40}Sb_{10}Se_{50}$, F_{ON} and F_{OL} values were estimated to be 4.7 MW/cm^2 and 38 MW/cm^2 quantifying the studied system for becoming an active optical limiter.

Viswanathan and Thomas [19] have explored the optical properties of Ag nanoparticle implanted $GeSeSb$ bulk and solution processed chalcogenide glasses. The solution processed glasses of different concentrations from $GeSeSb$ ($P_3=0.5 \text{ mg/ml}$, $P_4=1 \text{ mg/ml}$, $P_5=1.5 \text{ mg/ml}$) and $GeSeSbAg$ ($Q_3=0.5 \text{ mg/ml}$, $Q_4=1 \text{ mg/ml}$, $Q_5=1.5 \text{ mg/ml}$). The colloidal solutions were prepared by dissolving finely powdered samples in ethylenediamine. Then the thin films were prepared using the vacuum thermal evaporation. For both $GeSeSb$ and $GeSeSbAg$ bulk samples, the absorption edge shifted towards higher wavelength. The increase in size has been explained on the basis of increasing nanocluster size with rising concentration. Z-scan was utilized to study the NL behaviour of the glasses where a mode locked Nd:YAG laser was used generating 2nd harmonics at 532 nm at a pulse rate of 7ns and repetition rate 10 Hz. The necessary requirement for Z-scan experiments was satisfied with radius of beam waist, $\omega_0 = 42 \mu\text{m}$ and Rayleigh length, $z_0 = 10.7 \text{ mm}$ respectively [20]. In OA experiments (Laser Power = 246 MW/cm^2) RSA type transmittance valley was observed for all the studied compositions. In the resultant transmittance, a peak valley curve through a finite aperture confirmed self-defocusing behaviour and negative n_2 values which increased with increasing solute concentration. β decreased for both the samples i.e., from P_5 (17.233 cm/GW) to P_4 (11.827 cm/GW), and Q_5 (26.144 cm/GW) to Q_3 (10.213 cm/GW). The observed trend in β has been explained on the fact that increasing concentration, large size and number of solute particles [21,22] causes multiple

scattering and enhanced interaction length giving rise to higher nonlinear absorptions.

Moisset *et al* [23] have reported chalcogenide binary thin layers (Sb_2Te_3), which have been protected by silica, for super-resolution applications. The thin film of Sb_2Te_3 was deposited onto B270 multicomponent silicate glass substrate. The thin film was deposited *via* electron beam technique and a silica layer of 10 nm was deposited on them to shield the annealing effects. Silica has a transparency in the visible near infrared range and does not have a NLO response [24] making it a suitable material to be used for protecting layer of the thin films. The OA aperture traces have been taken at 1064 nm with incident laser energy per pulse 200 nJ and at 532 nm with incident laser energy per pulse 180 nJ for 24 nm thick annealed thin films. No nonlinearity was observed for as deposited thin films. The $\beta = -3.28 \pm 0.40 \times 10^{-3}$ m/W (11ns, 1064 nm) and $\beta = -5.85 \pm 1.20 \times 10^{-3}$ m/W (11ns, 532 nm). Although nonlinearity decreased by a factor of two in the NIR, the NLO parameters continued to remain significantly high, which is vital for Super-Resolution applications.

NLO properties of $\text{As}_{20}\text{S}_{80}$, low doped $\text{P}_2\text{As}_{20}\text{S}_{78}$ and $\text{Sn}_1\text{As}_{20}\text{S}_{79}$ have been investigated by Zou *et al* [25]. Sinter method was used to prepare the bulk samples and films were deposited by evaporation vacuum coating technology. In the Z-scan, a Nd:YAG laser radiation with $\lambda = 1064$ nm was used as the excitation source. The laser source had a repetition rate of 10 Hz, emitted linearly polarized 17 ps single pulses, and $\omega_0 \approx 65$ μm . The sample thickness was approximately 300 μm . In the CA z-scan mode valley-peak curves indicated positive nonlinearity in $\text{As}_{20}\text{S}_{80}$ films which led to the occurrence of self-focussing process. The n_2 values for $\text{As}_{20}\text{S}_{80} \approx 4.11 \times 10^{-14}$ cm^2/W , $\text{P}_2\text{As}_{20}\text{S}_{78} \approx 3.89 \times 10^{-14}$ cm^2/W and for $\text{Sn}_1\text{As}_{20}\text{S}_{79} \approx 4.68 \times 10^{-14}$ cm^2/W . So, n_2 increases with Sn doping while decreases with P addition to $\text{As}_{20}\text{S}_{80}$ system. From the OA z-scan mode β values (for $\lambda = 1.064$ μm , $I_0 = 2 \times 10^8$ W/cm^2) of $\text{As}_{20}\text{S}_{80}$, $\text{Sn}_1\text{As}_{20}\text{S}_{79}$ and $\text{P}_2\text{As}_{20}\text{S}_{78}$ thin films were measured to be $\sim 0.38 \times 10^{-9}$ cm/W , $\sim 0.31 \times 10^{-9}$ cm/W and $\sim 0.44 \times 10^{-9}$ cm/W respectively, implying a large NLA coefficient. The FOM for $\text{As}_{20}\text{S}_{80}$, P doped and Sn doped films was approximately 1.02, 0.83 and 1.42.

Cheruvath *et al* [26] reported the linear and NLO studies of $\text{Ge}_{20}\text{Se}_{70}\text{Te}_{10}$ nano colloids. Nano colloids were prepared in three different concentrations, Gc1 = 0.3 mg/ml, Gc2 = 0.5 mg/ml and Gc3 = 0.9 mg/ml. The powdered bulk samples were dissolved in synthesis grade ethanolamine. There is a band edge shift from bulk to solution form due to the size drop in glassy network. In the colloids, the absorption edge shows a red shift with an increase in concentration. It is reported that cluster size increases with increasing solution concentration [27]. The E_g values were estimated to be 3.28 eV, 3.2 eV, and 2.91 eV for Gc - 1, 2 and 3 respectively. For Gc3 the OA z-scans ($I_0 = 397$ MW/cm^2) indicate the presence of prominent RSA enabling the sample to become a suitable optical limiting applications material. However, there is no substantial NLA for Gc - 1 and 2 because the density of defect states around excitation wavelength is negligible. Moreover, the increased cluster size of Gc3 increased the light path length. This further increased the interaction between light and matter in the colloid enhancing the NLA in the concentrated sample. The CA scan has a peak to valley trend for all the systems under investigation implying a negative NL refractive index which varies inversely with the E_g values. Also, the existence of defect states lessens the FOM paving the route for NLA via a two-step photon absorption.

Sun *et al* [28] have correlated the structure of Ge-S binary system with its TONL properties. Authors prepared six GeS_x ($x = 1.6, 1.7, 1.9, 2, 4, 6$) chalcogenide glasses and examined them for

their NL properties using femtosecond (fs) Z-scan technique at $\lambda = 800$ nm. The testing wavelength (800 nm) was found to be distant from the fundamental absorption edge suggesting that TONL properties are non-resonant and have electronic origin. The E_g increased from 2.25 eV to 2.81 eV till $x = 4$ and then decreased to 2.79 eV for $x = 6$. The CA Z-scans of samples $x = 1.6, 1.7, 1.9$ possessed peak-following-valley configuration pointing at the self-focusing behaviour of GeS_x system under fs laser irradiance at 800 nm. This also signifies the positive values of n_2 which are decreasing with increasing S content. From the OA Z-scans it was evident that only two samples ($x = 1.6$ and 1.7) manifested the NA signal attributed to the RSA. Since the incident photon energy $> E_g/2$ so a TPA process has been assigned to the system with β of the order of 10^{-10} m/W for $x = 1.6$ and 1.7 sample which is significantly higher than Sb [29]- and Pb [30]-doped ternary or quaternary chalcogenide glasses based on Ge-S and As_2S_3 chalcogenide glass [12]. However, β values of Au [31]- and Ag [32]-doped Ge-S-derived chalcogenide glasses are two times higher than the studied system. The FOM $> 10 \pm 42$ % for the samples $x = 1.9$ to $x = 6$ and 0.52 ± 42 % and 0.64 ± 42 % for $x = 1.7$ and 1.6 respectively. $x = 1.6$ and $x = 1.7$ having large n_2 and β have been suggested for OL applications because they require robust TPA for protecting photonic devices.

Tintu *et al.* [33] have reported the NLO properties of nano colloidal solutions of concentrations $C_1 = 0.67$ mg/ml and $C_3 = 0.335$ mg/ml of $Ga_5Sb_{10}Ge_{25}Se_{60}$ in n-butylamine solvent. The E_g of bulk glass was found to be 1.56 eV while that of colloidal solution $C_1 = 2.50$ and $C_4 = 2.76$ eV. From the normalized transmittance curves in the OA scheme, non-linear absorption coefficient (β) values at $\lambda = 532$ nm for input laser power densities 182-539 MW/cm² were found to vary from 19.61 to 6.80 cm/GW for C_1 and 15.05 to 6.68 cm/GW for C_2 . This decrease in β values has been attributed to the removal of photocarriers, as the irradiation intensity increases, from the ground state. Authors suggested two-photon absorption to be the primary procedure involved in the NLA process. The optical limiting threshold values of $C_3 > C_1$ due to the enhancement of cluster size with the increase in concentration.

Fedus *et al* [34] discussed the impact of photoinduced effects (PIEs) on nonlinear refractive indices and β of the thin film $Te_{20}As_{30}Se_{50}$ using ps laser pulses at 1064 nm. The NL imaging technique with phase object (NIT-PO) and the Z-scan technique were employed. The results obtained from both the techniques were then compared. The NIT-PO (peak intensities: 1.2, 2.0, 2.8, and 3.3 GW/cm²) studies revealed that the oscillatory behaviour at 2.8 and 3.3 GW/cm² is related to phase shift values ascribed to TONL and to removal of holes occurring for each laser shot. CA and OA z-scan schemes were obtained at a laser intensity of 3.3 GW/cm² giving positive values of $n_2 = (9.0 \pm 1.4) \times 10^{-16}$ m²/W and $\beta = 760 \pm 80$ cm/GW. The z-scan experiment was repeated with low intensity laser and the results indicated that the sample acts as a divergent lens for low intensity having negative n_2 .

3. Conclusion

The nonlinear optical properties of various chalcogenide compositions like binary, ternary, quaternary etc. prepared via different techniques have been reviewed for the open aperture and closed aperture modes of Z-scan. Some special systems like colloidal chalcogenides and chalcogenide thin films coated with a protective layer have also been discussed. It has been observed that mostly

chalcogenide systems have a non-linear refractive index several orders greater than the conventional silica-based glasses. Generally, in the open aperture mode the nonlinear response is due to the two-photon absorption. On the other hand, in the closed aperture scheme peak-valley trend is observed which indicates at the self-focussing behaviour of the samples under laser irradiance. Chalcogenide glasses with large nonlinear refractive index and NLA coefficient values have been suggested for optical limiting applications because they require strong two photon absorption for protecting photonic devices.

4. References

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