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Investigation of nonlinear optical parameters of zinc based amorphous chalcogenide films

Sunita Rani*, Devendra Mohan, Nawal Kishore, Rakesh Dhar

Laser Laboratory, Department of Applied Physics, Guru Jambheshwar University of Science and Technology, Hisar 125001, Haryana, India

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ABSTRACT

Third order nonlinear optical properties of amorphous $Zn_x–S_y–Se_{100−x−y}$ chalcogenide films have been investigated using single beam transmission z-scan technique at 1064 nm of Nd:YAG laser. Measurement of optical properties of amorphous $Zn_x–S_y–Se_{100−x−y}$ chalcogenide films prepared by thermal evaporation technique has been made. X-ray diffraction patterns of chalcogenide films confirm the amorphous nature. Optical band gap (E_g) has been estimated using Tauc's plot method from transmission spectra that is found to decrease with increase in content due to valence band broadening and band tailing the system. Nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third order nonlinear susceptibility (χ^3) of chalcogenide films have been estimated. Self-focusing effect has been observed in closed aperture and reverse saturable absorption in open aperture scheme. Limiting threshold and dynamic range have been calculated from optical limiting studies. The increase in nonlinearity with increase in Zn content has been observed that is understood to be due to decrease in band gap on Zn doping. High nonlinearity makes these films a potential candidate for waveguides, fibers and two photon absorption in optical limiters.

1. Introduction

Chalcogenide glasses are nonoxide glasses containing sulphur, selenium and tellurium of the main group III–V elements. They exhibit amorphous semiconductor nature having energy band gap ranging from 1 to 3 eV. These glasses have excellent IR transmission from 0.5 to 16 μm, photosensitivity, high refractive index and high value of nonlinearity [1,2]. Chalcogenide glasses are used in real-time holography application due to photo structural modification effect and making refractive lenses due to IR transmission. These glasses have also wide applications in optical switching, fibers, optical imaging, laser power delivery, chemical sensing, imaging, scanning near field microscopy/spectroscopy, IR sources/lasers, realization of microstructures in integrated optics and amplifiers [3–5]. Glass is the most widely used material for fabricating a long fiber type waveguide. Due to low loss silica glass can be used but its low nonlinearity as compared to chalcogenide glass has made chalcogenide glass as promising material [6]. These applications and having good abilities to be obtained in amorphous thin film stimulate to study the optical properties of chalcogenide films. Optical properties of different chalcogenide films based with As, Ge, Cd, Zn, Pr, Dm and rare earth elements have been studied by various research workers [7–10]. It has been established that compositional variation leads to a change in optical band gap, refractive index and extinction coefficient [11,12].

Presently amorphous chalcogenide thin films of $Zn_x–S_y–Se_{100−x−y}$ have been prepared by thermal evaporation technique. Optical energy band gap have been evaluated by Tauc's plot of transmission spectra. Further third order refractive and absorptive nonlinearity exhibited by films has been studied using conventional z-scan technique.

2. Experimental

Bulk amorphous chalcogenide glasses have been prepared using vacuum sealed melt quenching method. The chemical elements constituting glass of high purity (99.999% purity) in appropriate quantity has been placed in a pre-cleaned quartz ampoule (length ~12 cm, inner diameter ~12 mm and outer diameter ~16 mm). The quartz ampoule is then sealed after evacuating to a pressure $\sim 10^{-3}$ torr by rotary pump. Sealed ampoule is heated in a furnace by gradually increasing temperature up to a range 875–925 °C depending upon the composition of sample and kept it for 24 h with frequently agitated to have homogeneous mixing of constituents. The quenching of melt has been done in ice cold water. After breaking of ampoule, ingot of glass has been grinded by mortar and pestle to make powder of prepared glass. Thin films of powdered glass have been obtained by thermal evaporation technique using high vacuum coating system at pressure of 10^{-6} torr.

* Corresponding author.
E-mail address: sgarhwal48@gmail.com (S. Rani).

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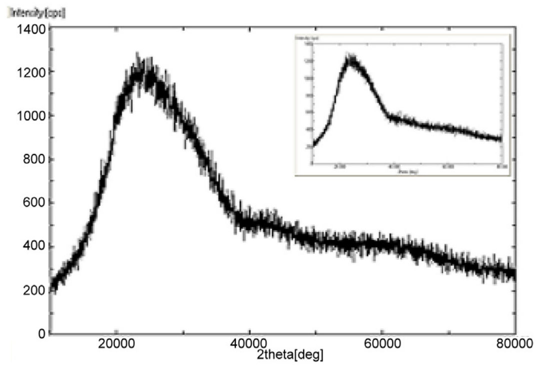

Fig. 1. Typical XRD pattern of chalcogenide $Zn_4S_{20}Se_{76}$ thin film.

X-ray diffraction patterns of films have been recorded using Rigaku X-ray diffractometer (Miniflex-II) to ascertain the amorphous nature as shown in Fig. 1 (inset showing XRD of $Zn_6S_{12}Se_{82}$ thin film). No sharp peak has been observed. Normal incidence optical transmission spectra have been obtained by a double beam ultraviolet–visible-infrared spectrophotometer (UV-3600) in wavelength range 400–1200 nm that predicts the IR transparency of these films as shown in Fig. 2. Optical band gap of these films have been estimated by Tauc's relation [11]

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

Here n can have values 2 and 1/2 in the case of indirect and direct transitions respectively, $h\nu$ is the photon energy, α is linear absorption coefficient and B is band tailing parameter. Fig. 3 shows plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ and indirect optical band gap of films can be obtained by extrapolation of the best-fit line between $(\alpha h\nu)^{1/2}$ vs $h\nu$ to intercept the $h\nu$ axis ($\alpha = 0$).

Nanosecond z-scan experiment in closed and open aperture configuration has been employed to distinguish refractive and absorptive nonlinearity. Nd:YAG (Quanta System, HYL-101) laser source of 1064 nm wavelength with Gaussian beam profile, 5 ns pulse width and repetition rate of 10 Hz has been used in z-scan as given elsewhere [13]. The sample has been moved along z-axis through the focal point of a lens of 15 cm focal length. The transmitted signal through an aperture of 4 mm in closed aperture configuration has been analyzed by Ophir detector (3A-FS-SH). Linear aperture transmittance (S) relates aperture radius (r_a) to beam radius (ω_a) through the relation $S = 1 - \exp(-2r_a^2/w_a^2)$ and $S < 1$ for closed aperture z-scan that is used to measure nonlinear refractive index whereas open aperture z-scan corresponds to $S = 1$ [14].

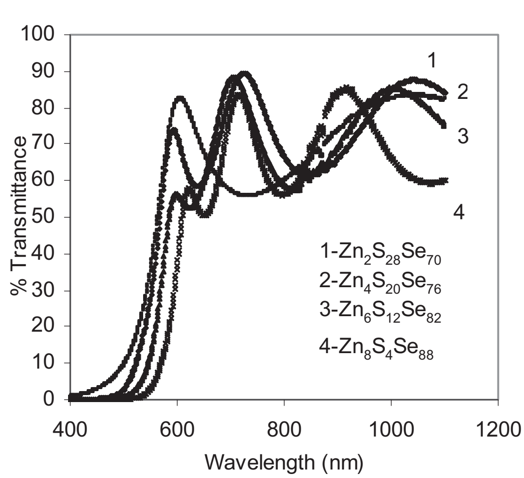

Fig. 2. Optical transmission spectra of amorphous chalcogenide films.

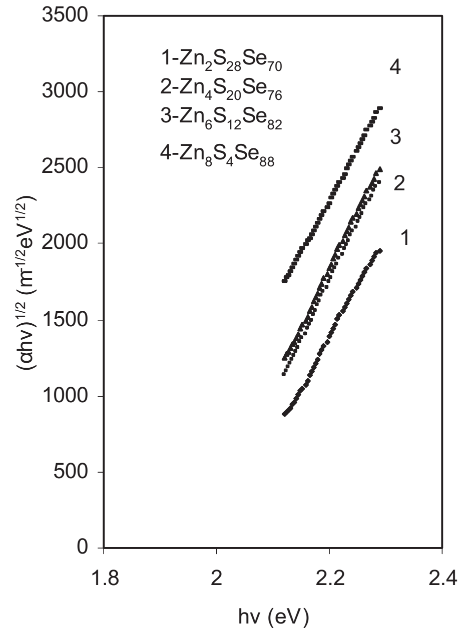

Fig. 3. Tauc's plot for Zn based chalcogenide films.

Optical limiting has been performed using open aperture with sample at focus and input power has been varied using attenuators.

3. Results and discussion

Table 1 shows optical band gap (E_g) obtained from above plot and there is a decrease in band gap with increase in Zn content due to valence band broadening and band tailing that is related to electronegativity of elements. For Se, S and Zn electronegativity values are 2.55, 2.58 and 1.65, respectively, and according to Kastner and Adler [15], lone pair p-orbitals are present in valence band of chalcogenide glasses that will have higher value of energies adjacent to electropositive elements than those of electronegative atoms. Therefore addition of electropositive Zn may raise the energy of lone pair states thereby broadening the valence band leading to band tailing and energy band gap decreases. Also with increase in Se element and decrease in S element that is more electronegative than Se that may decrease the band gap.

Further refractive indices (n_0) of the films under reference have been estimated using the relation [16]

$$n_0^4 E_g = 77 \quad (2)$$

The calculated values of n_0 have been presented in Table 1. The film thickness (d) is calculated by finding refractive indices n_1 and n_2 at two contiguous maxima or minima corresponding to wavelengths λ_1 and λ_2 and using the expression suggested by Sharma and Katyal [17]

$$d = \lambda_1\lambda_2/2(n_2\lambda_1 - n_1\lambda_2) \quad (3)$$

Fig. 4 shows normalized transmittance as a function of position in closed aperture configuration that evinces self-focusing effect (a pre-focal minimum followed by a post-focal maximum valley-peak) demonstrating positive value of nonlinear refractive index (n_2) for all films. Also the condition for self-focusing $\hbar\omega/E_g < 0.69$ has been contented [18]. For calculating nonlinear parameter n_2 the following relation has been used [19]

$$n_2 = |\Delta\varphi_0|/kL_{eff}I_0 \quad (4)$$

Here $|\Delta\varphi_0|$ is peak-on-axis phase shift, k is the wave number, L_{eff} is the effective thickness and I_0 is the intensity at focus.