CHAPTER 3

3.1 Introduction

Glasses with large optical nonlinearity have wide applications in nonlinear photonics, optical memory devices, IR optics and to tune the emission wavelengths of quantum cascade lasers [1-4]. Chalcogenide glasses possess large third order nonlinearity, high refractive index and exceptional transmission from visible to infrared region [5]. Due to high value of nonlinearity, these glasses have novel applications in fabricating waveguides and for all optical switching [6-8]. Cubic nonlinearity in a variety of oxide and non-oxide glasses has been investigated. Amorphous chalcogenides have larger nonlinearity than that of silica and oxide glasses [9]. These glasses show optical, electrical and structural changes when exposed to light or on ion irradiation [10, 11]. As a beam of energetic ions is incident on the surface of material, structural modification occurs depending on energy of ions [12]. The main processes that can occur on ion irradiation are ion implantation, damage, sputtering of surface atoms and mixing of substrate atoms with thin film atoms [13, 14]. Ion implantation leads to distribution of irradiated ions within the target solid material whereas structural damage to the material may be a result of hard nuclear collisions creating displacement of several atoms from regular sites. Due to nuclear collision one or more surface atoms can be ejected from surface creating sputtering of large number of target atoms [14]. The energy loss with penetration depth of energetic ions consists of nuclear and electronic energy loss. At low energy of ions, nuclear energy loss are dominating while electronic collisions occur for energies >1MeV [15]. Ions having energy of the order of MeV/nucleon or greater (swift heavy ions) interact with the electrons particularly through inelastic scattering thereby having good impact for the engineering of material as compared to low energy ions. Maninder Singh et al. [16] observed that optical properties of chalcogenide thin films have been influenced due to heavy ion irradiation. The change in optical properties of thin films can also effect the nonlinear optical properties of materials.

In the present work, the amorphous chalcogenide As$_2$S$_3$ films have been irradiated with Ge and Ni heavy ions to study the third order nonlinear optical properties. Transmission z-scan technique given by pioneer workers Sheik-Bahae et al. [17] has been proved to be simple and
highly sensitive technique to measure both the sign and magnitude of nonlinear refraction and nonlinear absorption, even when both nonlinearities are present simultaneously. Therefore, in the framework of the third order nonlinearity measurement of amorphous chalcogenide $\text{As}_2\text{S}_3$, $\text{As}_2\text{S}_3/\text{Ge(RT)}$, $\text{As}_2\text{S}_3/\text{Ge(LNT)}$ and $\text{As}_2\text{S}_3/\text{Ni(LNT)}$ thin films, z-scan technique is exploited using second harmonic of Nd:YAG laser. Further optical switching behaviour is realized and figures of merit are calculated.

3.2 Experimental Details

3.2.1 Sample Preparation

Bulk chalcogenide $\text{As}_2\text{S}_3$ glass is prepared by melt quenching technique and thermal evaporation technique is used to prepare chalcogenide $\text{As}_2\text{S}_3$ thin films of 0.5 $\mu$m thickness from bulk glass as described in Chapter 2. Ion irradiation is carried out using an NEC 16 MV Van de Graaff type Electrostatic Accelerator (Pelletron) at Nuclear Science Centre, New Delhi, India. Thin films are irradiated with Ge ions at room temperature and at liquid nitrogen temperature and with Ni ions at liquid nitrogen temperature of 75MeV/nucleon energy at a fluence of $1\times10^{13}$ ions/cm$^2$. Ion beam having 10-14nA current is defocused so that whole surface of thin film of 10×10 mm$^2$ area is irradiated with uniform ion dose.

3.2.2 Optical Z-Scan Set-up

Single beam z-scan technique has been used to monitor the cubic nonlinear optical parameters viz. nonlinear refractive index ($n_2$), nonlinear absorption coefficient ($\beta$) and third order nonlinear susceptibility ($\chi^{(3)}$). In z-scan experimental set-up as shown in Chapter 2, second harmonic of Nd: YAG laser (Quanta System, HYL-101) with Gaussian beam of 5ns pulse width and repetition rate of 10Hz has been focused by focal lens of 15cm focal length.

3.3 Results and Discussion

3.3.1 X-ray Diffraction

To study the change in material structure on heavy ion irradiation, x-ray diffraction pattern is recorded using Rigaku X-ray diffractometer (Miniflex-II) and XRD patterns are
presented in Figure 3.1. The high intense peak at $2\theta \approx 26.66^0$ in Figure 3.1 (a) corresponds to formation of c-NiS$_2$ with Ni ion irradiation that is confirmed from ICDD database PDF-2 (00-003-0734). The sharp peak at $2\theta \approx 26.82$ (Figure 3.1 (b)), and at $2\theta \approx 26.40$ (Figure 3.1 (c)) are due to Germanium as depicted in ICDD database PDF-2 (00-003-0478). The other peaks in Figure 3.1 indicate that crystallization is induced in amorphous chalcogenide thin film with heavy ion irradiation [18].
3.3.2 Optical Band Gap

Values of optical band gap energy \( E_g \) have been calculated using Tauc’s plot of \( (\alpha_0 h\nu)^{1/2} \) versus \( h\nu \) of transmission data measured by UV-VIS-NIR spectrophotometer as shown in Figure 3.3 [19]. According to Tauc and A. Menth [19], the plot of linear absorption coefficient \( \alpha_0 \) vs. \( h\nu \) (Figure 3.2) can be divided into three parts for amorphous materials.

Figure 3.1 X-ray diffraction traces of (a) As\(_2\)S\(_3\)/Ni(LNT) (b) As\(_2\)S\(_3\)/Ge(RT) and (c) As\(_2\)S\(_3\)/Ge(LNT) thin films
Figure 3.2 Three parts of absorption edge in amorphous materials

Part A corresponds to very low absorption $\alpha_0 < 1\text{ cm}^{-1}$ that has exponential shape and mainly depends on structure and purity of sample.

In part B, value of $\alpha_0$ lies in the range $1 < \alpha_0 < 10^4\text{ cm}^{-1}$ and $\alpha_0 \sim \exp\left(\frac{h\nu}{E_\text{c}}\right)$, value of $E_\text{c}$ is between 0.05 and 0.08eV at and below room temperature.

Part C has $\alpha_0 > 10^4\text{ cm}^{-1}$ indicating transitions to be the type of $\alpha_0 h\nu \sim (h\nu - E_\text{g})^n$, $n$ can have values 1/2, 2 and 3. For amorphous materials, $n = 2$ has been observed indicating indirect transitions between extended states of valence and conduction bands [20, 21, 22]. The value of...
optical band gap \( (E_g) \) can be obtained by extrapolation of linear part to intercept the energy axis.

For ion irradiated chalcogenide thin films \( \text{As}_2\text{S}_3/\text{Ge}(\text{LNT}), \text{As}_2\text{S}_3/\text{Ge}(\text{RT}) \) and \( \text{As}_2\text{S}_3/\text{Ni}(\text{LNT}) \), the calculated values of \( E_g \) are 1.9, 1.925 and 2.10 eV, respectively, whereas for unirradiated \( \text{As}_2\text{S}_3 \) films the value is 2.34eV [23]. This decrease in band gap is due to the increase in the localized states within the band gap of \( \text{As}_2\text{S}_3 \) films on ion irradiation as given by Davis and Mott [11].

![Graph of absorbance vs. energy](image-url)
Figure 3.3 Tauc’s plot of (a) As$_2$S$_3$/Ni(LNT) (b) As$_2$S$_3$/Ge(RT) and (c) As$_2$S$_3$/Ge(LNT) thin films

3.3.3 Nonlinear Characterization

Using z-scan technique, nonlinear refractive index, nonlinear absorption coefficient and third order nonlinear susceptibility as mentioned in Chapter 2 are calculated. Figure 3.4 shows that self-defocusing effect (peak followed by valley) in As$_2$S$_3$/Ge(LNT) thin film indicating $n_2 < 0$ and self-focusing (valley followed by peak) in As$_2$S$_3$/Ge(RT) and As$_2$S$_3$/Ni(LNT) films representing $n_2 > 0$ have been observed experimentally. The calculated values of $n_2$ for
As$_2$S$_3$/Ge(RT), As$_2$S$_3$/Ge(LNT) and As$_2$S$_3$/Ni(LNT) thin films comes out to be $1.2 \times 10^{-13}$, $5.3 \times 10^{-13}$ and $1.4 \times 10^{-13}$ cm$^2$/Watt respectively.
Figure 3.4 Closed aperture Z-scan curve for (a) As$_2$S$_3$/Ge(LNT) (b) As$_2$S$_3$/Ge(RT) and As$_2$S$_3$/Ni(LNT) chalcogenide films

In open aperture z-scan curves, shown in Figure 3.5 saturable absorption has been observed. The values of $\beta$ obtained for As$_2$S$_3$/Ge(RT), As$_2$S$_3$/Ge(LNT) and As$_2$S$_3$/Ni(LNT) thin films are $1.0 \times 10^{-8}$, $9.6 \times 10^{-8}$ and $8.9 \times 10^{-9}$ cm/Watt, respectively.
Figure 3.5 Open aperture z-scan curve for (a) As$_2$S$_3$/Ge(LNT) (b) As$_2$S$_3$/Ge(RT) and (c) As$_2$S$_3$/Ni(LNT) chalcogenide films
For As$_2$S$_3$/Ge(RT), As$_2$S$_3$/Ge(LNT) and As$_2$S$_3$/Ni(LNT) thin films, values of calculated $\chi^{(3)}$ are $6.5 \times 10^{-15}$, $6.3 \times 10^{-15}$ and $5.7 \times 10^{-15}$ esu respectively that shows higher nonlinearity in ion irradiated films as compared to virgin As$_2$S$_3$ thin film given elsewhere [23]. There is increase in nonlinearity due to decrease in band gap on ion irradiation as suggested by B. S. Wherrett [24] wherein $\chi^{(3)}$ is inversely proportional to optical band gap energy $E_g$.

Optical switching experiment has been performed at 532nm wavelength and input intensity has been varied using attenuators. Figure 3.6 clearly depicts the optical switching behaviour of films, wherein increase in input intensity causes normalized output transmission to switches to a low value and relative switching fraction of approximately 70% is achieved. Optical switching property of chalcogenide thin film can be used in integrated asymmetric Mach-Zehnder interferometer wherein the light is divided unequally between two arms of interferometer [25]. The incident light induces the phase change due to intensity dependent refractive index. Important feature of Interferometer device is that it requires the half phase change as compared to nonlinear directional coupler device.

Figure 3.6 Optical switching behavior as a function of input intensity in chalcogenide thin films
Two figures of merit for optical switching are $W$ and $T$ given by [26]

$$W = \frac{n_2 I}{\alpha_0 \lambda}$$

$$T = \frac{\beta \lambda}{n_2}$$  \hspace{1cm} (3.2)

For $\text{As}_2\text{S}_3/\text{Ge(LNT)}$ thin film, calculated values of $W = 1.7 > 1$ and $T = 0.9 < 1$ satisfy the condition for photonic switching [26]. Also the condition of two photon absorption (TPA) is eliminated that prohibits the power loss in integrated nonlinear directional couplers (NLDC) for optical switching applications [27].

$$E_g < 2\hbar \omega < 2E_g$$  \hspace{1cm} (3.3)

Table 3.1 Cubic nonlinear optical parameters of irradiated films at 532nm in nanosecond regime.

<table>
<thead>
<tr>
<th>Nonlinear parameter</th>
<th>$\text{As}_2\text{S}_3$</th>
<th>$\text{As}_2\text{S}_3/\text{Ge(LNT)}$</th>
<th>$\text{As}_2\text{S}_3/\text{Ge(RT)}$</th>
<th>$\text{As}_2\text{S}_3/\text{Ni(LNT)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_2$ \hspace{1cm} $10^{-14} \text{cm}^2/\text{watt}$</td>
<td>5.9</td>
<td>53</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>$\beta$ \hspace{1cm} $10^{-9} \text{cm/watt}$</td>
<td>4.5</td>
<td>9.6</td>
<td>10</td>
<td>8.9</td>
</tr>
<tr>
<td>$\chi^{(3)}$ \hspace{1cm} $10^{-15} \text{esu}$</td>
<td>2.8</td>
<td>6.3</td>
<td>6.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>

3.4 Inference

Third order nonlinear optical parameters viz. nonlinear refractive index ($n_2$), nonlinear absorption coefficient ($\beta$) and third order nonlinear susceptibility ($\chi^{(3)}$) of $\text{As}_2\text{S}_3/\text{Ge(RT)}$, $\text{As}_2\text{S}_3/\text{Ge(LNT)}$ and $\text{As}_2\text{S}_3/\text{Ni(LNT)}$ thin films are calculated. From comparative study of third
order nonlinear parameters, higher nonlinearity is observed in Ge ion irradiated As$_2$S$_3$
chalcogenide film at liquid nitrogen temperature due to decrease in band gap. High value
of nonlinearity, good figure of merit and absence of two photon absorption predict the wide
application of As$_2$S$_3$/Ge(LNT) film in nonlinear optics, nonlinear directional couplers, optical
switching and photonics.
References


