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Non-linear refractive index of *a*-Ge-Se-In-Bi glassy thin films

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ABSTRACT

To explore the potentialities of chalcogenide glasses for ultrafast optical switching, in this paper we report the measurements of non-linear refractive index of amorphous $Ge_{20}Se_{70-x}In_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) chalcogenide glasses. The formulation proposed by Fournier and Snitzer has been used to predict the non-linear behavior of Ge-Se-In-Bi system. The linear refractive index and Wemple-DiDomenico parameters were used for the determination of nonlinear refractive index in the wavelength region 400 to 1500 nm. This is observed that non-linear refractive index increases linearly with increasing linear refractive index. Non-linear refractive indices, three orders higher than silica glass, have been obtained in the ternary system. Third-order optical nonlinear susceptibilities ($\chi^{(3)}$) has also been evaluated from changes of index of refraction using Wang approximations. The addition of Bi drastically increases the non linear refractive index. We examined the dependence of susceptibility on the absorption edge, thereby showing that the susceptibility rapidly increases with the red shift in absorption edge. Comparison of our results shows a good agreement with values available in the literature at 1.55 eV.

Key words: Non-linear refractive index, Ge-Se-In-Bi, Glass, Thin films.

INTRODUCTION

Interest in nonlinear behavior of optical materials arises from their application in high-power laser systems since the refractive index becomes intensity dependent when exposed to high electric fields. Nonlinear refraction is used to obtain optical limiting behavior. The development of nonlinear optical (NLO) materials has gained much impetus from their wide application ever since the first observation of optical second harmonic generation (SHG). Ultrafast all-optical switching using highly nonlinear optical waveguides is desirable for future high-speed optical signal processing. The major property of interest is that of non-linear refractive index of the crystals. Because of this non-linear refractive index, a Gaussian beam propagating through the crystals induces a lens-like refractive index profile. The refractive index change in turns modifies the beam propagation. It is important to understand this lensing effect in order to better use the material in optical system applications. Various methods exist to predict the nonlinear refractive index as discussed in [1]. For telecommunications based applications, these glasses stand out because they also exhibit third-order optical nonlinearities between two to three orders of magnitude greater than silica. This property has gained increasing recognition and has lead to a number of recent demonstrations of all-optical processes including switching [2], regeneration [3-5], wavelength conversion [6,7], amplification [8], lasing [9] etc.

The non linear effects can be found in many crystals, but the glasses have advantage over crystal in lower cost, better processing, very often in larger refractive non-linearity and in the possibility to include them easily into optical fibers and planer waveguide. Glasses containing highly polarizable atoms or ions were expected to have large non-linear optical properties; namely the chalcogenides (S, Se, Te) have become very interesting [10].

Chalcogenide glasses have been attracted recently a substantial interest as they have highest linear and non-linear refractive index amongst glasses resulting in highest non-linear properties and are of significance in advancing the next generation photonic chip platform for ultrafast all-optical signal processing.

Glasses with $E_g^{opt} \approx 1.6\,\text{eV}$ are promising for nonlinear applications. Accordingly, the material with $E_g^{opt} \approx 1.6\,\text{eV}$ is suitable to optical devices which are utilized at the communication wavelengths of $\lambda = 1.3 - 1.5\,\mu\text{m}$ $(h\nu \approx 0.8\,\text{eV})$ [11]. This spectral insight can be applied as a rough approximation also to non-crystalline semiconductors having non-direct gaps [12]. When considering optical nonlinearity in homogeneous media, we should take spectral dependence into account. The transmission spectra of thin films have been analyzed.

In the present work we have calculated the nonlinear refractive index and susceptibility in $Ge_{20}Se_{70-x}In_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) thin films and have considered the possible behavior of non-linear refractive index with film composition and have examined how the non-linear refractive index behaves with linear refractive index. Liner refractive index of Ge-Se-In-Bi vacuum evaporated amorphous thin films has already been reported using transmission spectra in the spectral range of 400-1500 nm having indirect gaps of E_g^{opt} [13, 14]. These films are of interest as a possible application in nonlinear optics. A Comparison of the calculated results has also been given with different materials whose nonlinear refractive indices were reported either theoretically or by different methods.

MATERIALS AND METHODS

Thin films of $Ge_{20}Se_{70-x}In_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) chalcogenide system were prepared by thermal evaporation technique [Vacuum coating unit HINDHIVAC 12A4D Model] at room temperature and base pressure of ~10^{-4} Pa. The stoichiometry of evaporated samples were checked by an electron microprobe analyzer (JEOL 8600 MX) on different spots (size ~ 2 µm) indicated that their composition was in good coincidence (± 1-2%) with that of the glass material used for evaporation. Amorphous nature of thin films was checked by XRD technique. The linear refractive indices used herein were obtained from the normal incidence transmission spectra of $Ge_{20}Se_{70-x}In_{10}Bi_x$ thin films obtained by a double beam ultraviolet-visible-near infrared spectrophotometer [Perkin Elmer Lambda 750] in the transmission range 400-1500 nm. All optical measurements were performed at room temperature (300 K).

RESULTS AND DISCUSSION

XRD studies were carried out in order to get an idea of the structural changes produced in $Ge_{20}Se_{70-x}In_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) bulk samples and their corresponding thin films as a result of the increase of Bi content at room temperatures. Absence of sharp peaks confirms that both the bulk samples and as-deposited films were amorphous in nature.
When matter is exposed to intense electric fields, polarization is no longer proportional to the electric field and the change in polarizability has to be extended by terms proportional to the square of the electric field. For the refractive index Δn can be expressed as:

$$\Delta n = n_2 <E>^2 \tag{1}$$

where n_2 is the non-linear refractive index and $<E>^2$ is the time-averaged electric field of the optical beam. Fournier and Snitzer [15] have proposed a formula for calculating the non-linear refractive index (n_2) of the corresponding films and is calculated using relation;

$$n_2 = \frac{(n^2+2)^2(n^2-1)}{48\pi n N}\frac{E_d}{(E_0)^2} \tag{2}$$

where n is linear refractive index, N is the density of polarizable constituents, E_o and E_d are Wemple-DiDomenico dispersion parameters determined from the experimental data by using single-oscillator relation [16]

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (h\nu)^2} \tag{3}$$

Dependence of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ is often linear. Plotting $(n^2-1)^{-1}$ against $(h\nu)^2$ (not shown here) allows us to determine the oscillator parameters by fitting a straight line to the points. The values of E_0 and E_d can be directly determined from the slope $(E_0 E_d)^{-1}$ and the intercept on the vertical axis (E_0/E_d).

In order to estimate the non-linear refractive index by applying equation (1) & (2), linear refractive index was measured for all the investigating spectral range. The calculated values of E_0 and E_d are given in table 1 [14]. The values of E_0 and E_d are further used in equation (2) to determine n_2. The calculated values of refractive index at 800 nm are tabulated in table 2.

Table-1

x	E_d (eV)	E_0 (eV)	ρ (g/cc)	V_m (cc)
0	54.22	7.15	4.2	19.35
2	35.78	4.44	4.65	18.03
4	32.76	3.96	4.84	17.85
6	34.21	3.92	5.07	17.56
8	33.67	3.72	5.23	17.51
10	32.69	3.54	5.44	17.30

Table 2

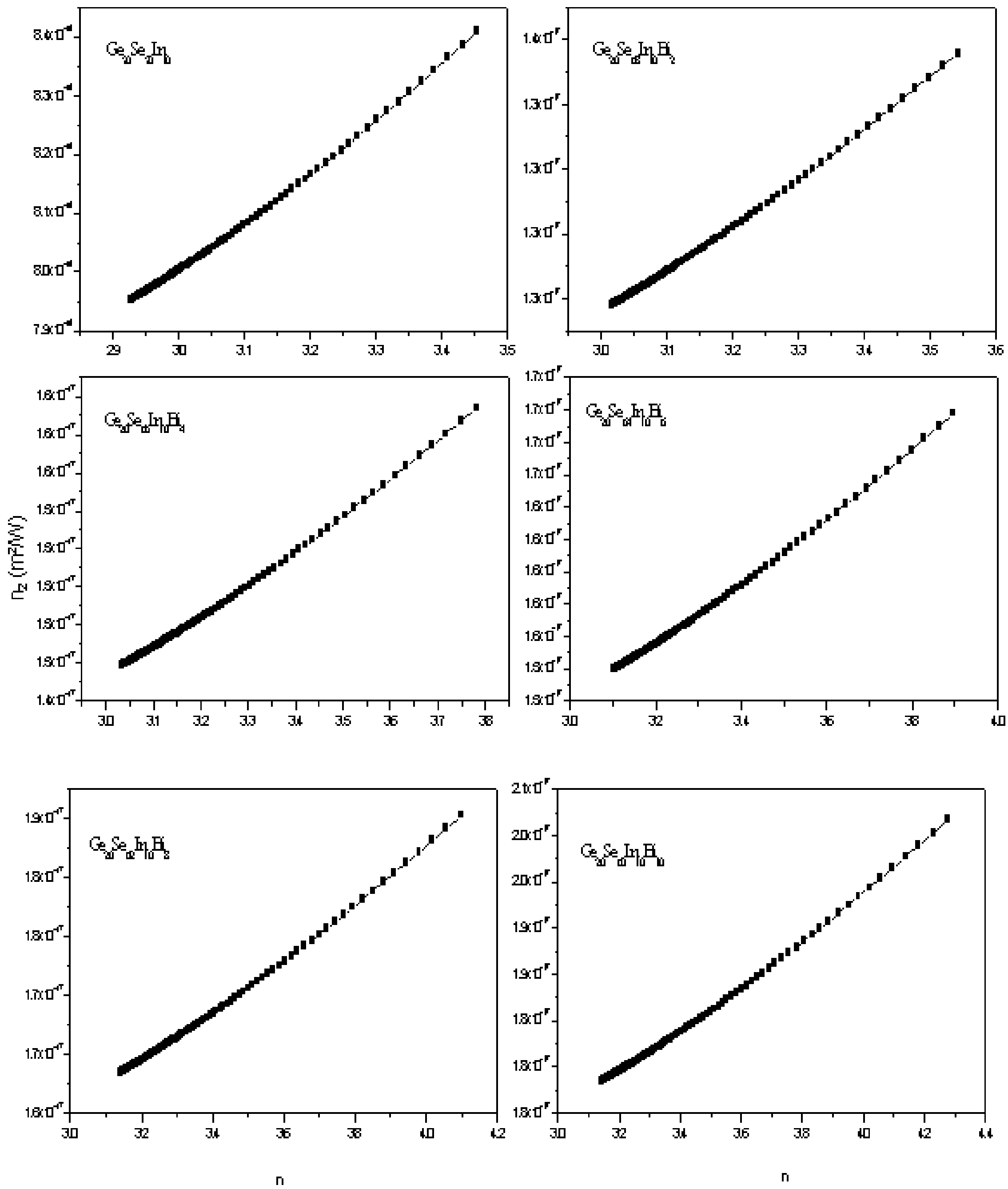
x	n	Nonlinear Refractive Index at 1.55 eV (m^2/W)	Susc. (esu)	References
0	3.09	0.8×10^{-17}	1.16×10^{-10}	Present
2	3.18	1.29×10^{-17}	1.98×10^{-10}	Present
4	3.26	1.49×10^{-17}	2.41×10^{-10}	Present
6	3.35	1.58×10^{-17}	2.69×10^{-10}	Present
8	3.44	1.74×10^{-17}	3.12×10^{-10}	Present
10	3.5	1.86×10^{-17}	3.44×10^{-10}	Present
Silica	-	2.2×10^{-20}	2.8×10^{-14}	[23]
Ta_2O_5	-	7.23×10^{-19}	-	[24]
$As_{38}S_{62}$	2.6	4×10^{-18}	1.1×10^{-11}	[25]
Fluoride-phosphate glass	-	2.05×10^{-20}	7×10^{-12}	[26]
Photo-thermo refractive glass	-	3.3×10^{-20}	-	[27]
As_2S_3	-	2.92×10^{-18}	0.67×10^{-12}	[23]
As_2Se_3	-	1.2×10^{-17}	-	[23]
$GeSe_4$ ($Ge_{20}Se_{80}$)	……..	9×10^{-18}		[28]
Bi_2O_3		1.10×10^{-18}		[23]
NaF			9.4×10^{-14}	[29]
$As_{40}S_{57}Se_3$			1.1×10^{-11}	[30]

Figure 1 represents the variation of nonlinear refractive index (data calculated from equation 2, using the *n* values and the data given in Table 1) versus linear refractive index (n) for all the samples. This is clear from the figure, the nonlinear refractive index increases with increase in linear refractive index. Also n_2 follows the same trend as n follows with photon energy (wavelength) [14] *i.e.* with the increase of wavelength it decreases for all the compositions. Composition dependent non-linear refractive index values at 800 nm wavelength are given in table 2.

The compositional behavior of n_2 is similar to that observed for n *i.e.* with the increase of Bi content non linear refractive index is also increasing for the investigated wavelength range. As is observed, the compositions with small oscillator energy have larger n_2 values. In general, lower the linear refractive index and wider the forbidden energy gap, smaller the optical nonlinearity. Our results also show the same tendency. Optical gap has already been reported and it decreases with the increase of Bi content [14]. We can also make this conclusion on the basis of E_0 values according to Tanaka relation [17] *i.e.* $E_0 \approx 2 \times E_g^{opt}$.

Non-linearity are determined largely by the abundance of most polarizable constituents. Non linear refractive index increases as the band gap decreases in selenides glasses [18].

Fig.1. Variation of nonlinear refractive index versus linear refractive index (n)



This behavior can be explained presumable due to the increased polarizability [19] associated with the larger Bi atom. Larger the atomic radius of the atom, larger will be its polarizability and consequently, according to Lorentz-Lorenz relation [20], larger will be the refractive index.

$$\frac{n^2-1}{n^2+2}=\frac{1}{3\varepsilon_0}\sum_i N_i\alpha_{pi} \tag{4}$$

where ε_0 is the vacuum permittivity, N_i is the number of polarizable units of type i per unit volume with polarizability α_{pi}. The atomic radius of Se is 1.16 A^o and that of Bi is 1.46 A^o. This increase in the linear refractive index with increase of Bi content may be ascribed to the addition of heavier Bi (density = 9.8 g/cc at 20 ^{o}C) atoms to Se (density = 4.79 g/cc at 20 ^{o}C) matrix leading to make the system more compact.

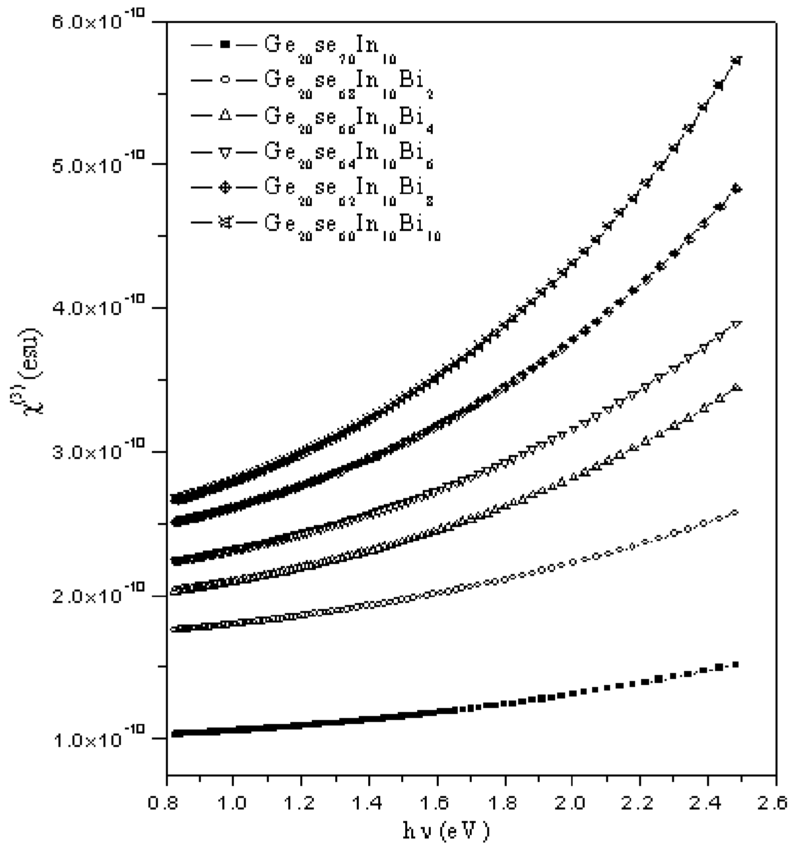


Fig. 2. Variation of susceptibility with energy

Third-order non-linear susceptibility as a dominant non-linearity in all glassy materials, is produced by excitation in the transparent frequency region well below the band gap E_g^{opt}. A relation between the linear and third-order nonlinear susceptibility involving an average energy gap and a single oscillator-strength parameter has been proposed by Wang [21]. Using energy gap and oscillator-strength parameters determined by Wemple and DiDomenico by fitting the dispersion of the linear index to a single-oscillator model [16], Wang finds reasonable agreement between predicted and measured values of n_2 for a wide variety of materials. n_2 is related to the third-order susceptibility $(\chi^{(3)})$ by the relationship :

$$n_2 = (2\pi / n)\chi^{(3)} \quad (5)$$

Figure 2 shows the variation of susceptibility with energy for $Ge_{20}Se_{70-x}In_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) thin films. Composition dependent third-order susceptibility values at 800 nm wavelength are given in table 2. With the increase in Bi content, $\chi^{(3)}$ increases. $\chi^{(3)}$ generally increases monotonically with decreasing optical band gap and with increasing density. In the present glasses same trend has been shown [22] which can be further satisfied by the increase in refractive index values with the increase in Bi content.

The values of nonlinear refractive index for $Ge_{20}Se_{70-x}In_{10}Bi_x$ thin film are compared with other materials in table 2. This is clear from the values given in table that the material under investigation has higher value by two to three orders while is comparable with values tabulated.

Now the question could have a practical importance, because the large the non-linearity, the lower is the necessary power and shorter is the interaction lengths required for possible applications.

CONCLUSION

Nonlinear refractive index of $Ge_{20}Se_{70-x}In_{10}Bi_x$ (x = 0, 2, 4, 6, 8, 10) thin films has been determined using Fournier and Snitzer formulation based on Wemple-DiDomenico single oscillator parameters. Nonlinear refractive index increases linearly with linear refractive index. With the increase in Bi content both non linear refractive index and $(\chi^{(3)})$ increases. This is found that non-linear refractive index for $Ge_{20}Se_{70-x}In_{10}Bi_x$ system is of three orders higher than silica glass. So the $Ge_{20}Se_{70-x}In_{10}Bi_x$ may be used as an optical material for high speed communication fibers.

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