

# New Quaternary Sb-Se-Ge-In Chalcogenide Glasses: Linear and Nonlinear Optical Properties

SUNANDA SHARDA,<sup>1,2</sup> NEHA SHARMA,<sup>1</sup> PANKAJ SHARMA,<sup>1,3</sup>  
and VINEET SHARMA<sup>1,4</sup>

1.—Department of Physics and Materials Science, Jaypee University of Information Technology, Waknaghat, Solan 173234, Himachal Pradesh, India. 2.—e-mail: sunandasharda@gmail.com. 3.—e-mail: pks\_phy@yahoo.co.in. 4.—e-mail: vineet.sharma@juit.ac.in

Chalcogenide glasses find extensive applications in infrared (IR) devices and optical communication. Optical parameters of  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  thin films, deposited by the thermal evaporation technique, have been analyzed using ultraviolet–visible–near IR spectroscopy. The transitions in the forbidden gap are indirect. The effect of indium (In) alloying on the nonlinear optical parameters has been studied. A shift in optical absorption edge towards higher wavelength shows that the width of the localized states changes, which affects the optical parameters of the system. The high nonlinearity of these glasses makes them suitable for optical regeneration and Raman amplification.

**Key words:** Chalcogenides, thin films, optical properties

## INTRODUCTION

Ultrafast all-optical switching devices play an important role in the field of signal transmission requiring high speeds and bit rates.<sup>1</sup> Silica glass optical fibers have low loss and high interaction length, which makes them favorable for fiber communication.<sup>2,3</sup> However, the low nonlinear refractive index of silica requires a high switching power and a very long length of fiber.<sup>3</sup> Chalcogenide glasses have nonlinearity several orders greater than silica<sup>4</sup> and thus ultrafast response time.<sup>4</sup> SbSeGe materials are promising for use in infrared (IR) optical fibers not only due to their high transparency in the IR region but also because of their wide bandgap, low material dispersion, low light scattering, and long-wavelength multiphonon edge.<sup>5,6</sup> For 25 at.% Ge alloying in  $\text{Sb}_{10}\text{Se}_{90-x}\text{Ge}_x$  glass alloys, an optimal glass-forming composition is obtained with minimum light scattering losses.<sup>7,8</sup> However, a composition with higher percentage of Ge also becomes more prone to crystallization.<sup>9</sup> Therefore, the Ge concentration has been reduced in  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25}$  by alloying with indium (In). It has been reported that In addition increases the dark

conductivity due to an increase in the number of defect states<sup>10</sup> and decreases the thermal activation energy<sup>11</sup> of the system. Glasses with In content are promising for nonlinear applications and are suitable for optical devices.<sup>12</sup> Therefore, In has been chosen as an additive because, being a metal, it is expected that it may decrease the bandgap of the material.<sup>13</sup> Also, In-Se binary glassy alloys are interesting materials for solar cell applications.<sup>14</sup> Currently, In-based chalcogenides have attracted significant attention due to their potential applications in smart digital electronic devices.<sup>15</sup> These devices rely upon nonvolatile memory that uses the reversible phase transition of chalcogenide resistors.<sup>15</sup> So, In has been chosen as a dopant to study its effect via optical transmission measurements.

In the present study, an effort has been made to study the effect of increasing In concentration on the linear and nonlinear optical properties of  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  ( $y = 0, 3, 6, 9, 12, 15$ ) glasses. Replacement of In by Ge, with a higher density, may increase the linear refractive index ( $n$ ) and hence the nonlinearity of the glasses. The refractive index ( $n$ ) and extinction coefficient ( $k$ ) have been evaluated using Swanepoel's envelope method.<sup>16</sup> The optical bandgap ( $E_g^{\text{opt}}$ ) has been correlated with the absorption coefficient ( $\alpha$ ) and oscillator energy ( $E_0$ ). The ratio of the charge carrier concentration to the

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effective mass ( $N/m^*$ ), the third-order nonlinear susceptibility [ $\chi^{(3)}$ ], and the nonlinear refractive index ( $n_2$ ), using the Tichy and Ticha<sup>17</sup> and Fournier and Snitzer approaches,<sup>18</sup> have also been calculated.

### EXPERIMENTAL PROCEDURES

Bulk samples of  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  ( $y = 0, 3, 6, 9, 12, 15$ ) glasses were prepared using the melt-quench technique. The detailed experimental procedure is given elsewhere.<sup>8</sup> The amorphous nature of the samples was confirmed by x-ray diffractometry (X'Pert PRO) showing no prominent peak (not shown here). Thin films of these bulk samples were deposited using the vacuum evaporation technique, and the composition of the thin films was verified by electron probe microanalysis (EPMA; JEOL 8600 MX) at different spots (size  $\sim 2 \mu\text{m}$ ) for compositional analysis. EPMA is a microbeam technique used primarily for nondestructive chemical analysis of minute solid samples. The compositional elements (Sb, Se, Ge, and In) and the quenched samples were taken as reference and found to be uniform within accuracy of about  $\pm 1.5\%$  to  $\pm 2\%$ . The transmission spectra of the deposited films were obtained using a double-beam UV-Vis-NIR spectrophotometer (Lambda 750; PerkinElmer) in the spectral range from 500 nm to 2500 nm with slit width of 1 nm at room temperature (300 K).

### RESULTS AND DISCUSSION

The transmission spectra for the  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  ( $y = 0, 3, 6, 9, 12, 15$ ) thin films (Fig. 1) show a shift of the absorption edge towards higher wavelength, indicating a red-shift.

The values of  $n$  and  $k$  were calculated using the Swanepoel method.<sup>16</sup> The complex refractive index for uniform thickness is given by  $n^* = n - ik$ . The value of  $k$  is related to the absorption coefficient in

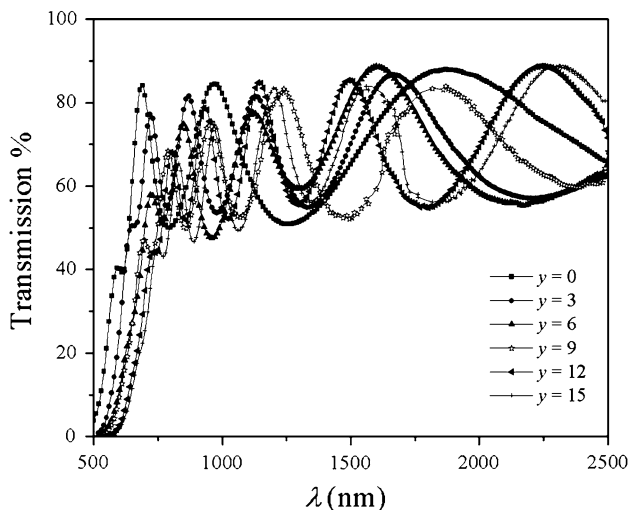


Fig. 1. Transmission spectra of  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  thin films.

the strong absorption region as  $k = \alpha\lambda/4\pi$ . It can be observed from Fig. 2a that  $n$  decreases with increasing wavelength, showing normal dispersion. With In addition,  $n$  increases, which can be explained using the Lorentz-Lorenz relation.<sup>19</sup> According to this relation, the larger the atomic radius, the greater the polarizability and hence the larger the refractive index. Since, Ge (1.22 Å)<sup>20</sup> is being replaced by larger In (1.50 Å)<sup>20</sup> atoms, there is an increase in the value of  $n$ . Also, a red-shift in the transmission spectrum must necessarily give an increased value of refractive index, according to the fundamental Kramers-Kronig relation.<sup>19</sup> The value of  $k$  increases with increasing wavelength (Fig. 2b), indicating that there is an increase in the fraction of light scattered in the interference-free region. The high  $n$  values of this glassy system suggest that the material can be used to create high-refractive-index contrast between layers of quarter-wave stacks for omnidirectional reflection.<sup>21</sup> This could further be used for making IR mirrors and filters.<sup>21</sup>

The optical bandgap was determined from the relation proposed by Tauc and Wood,<sup>22</sup>

$$\alpha h\nu = B(h\nu - E_g^{\text{opt}})^p \quad (1)$$

The nonlinear nature of the curves (Fig. 3) confirms that the transitions occurring in the forbidden gap are indirect, most likely due to the lack of translational symmetry in chalcogenides. The intercept on extrapolation to the energy axis gives the value of  $E_g^{\text{opt}}$ . The value of  $E_g^{\text{opt}}$  decreases with increasing In concentration (Table I). With addition of In into  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25}$ , stronger Ge-Se bonds are replaced by In-Se bonds and unsaturated Se-Se bonds are also formed. Unsaturated Se-Se bonds give rise to defect states, producing localized states which are responsible for the decrease in  $E_g^{\text{opt}}$ . The free charge carrier concentration ( $n_\sigma$ ) was also calculated, using the equation<sup>10</sup>

$$n_\sigma = 2 \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \exp \left( \frac{-\Delta E_\sigma}{k_B T} \right) \quad (2)$$

where  $m$  is the mass of a charge carrier,  $k_B$  is the Boltzmann constant, and  $\Delta E_\sigma$  is the activation energy, which is nearly half of  $E_g^{\text{opt}}$ . The value of  $n_\sigma$  increases with increasing In concentration. These charge carriers act as localized states,<sup>10</sup> thereby decreasing  $E_g^{\text{opt}}$ . The value of  $\alpha$  can be correlated to  $E_g^{\text{opt}}$  on the basis of the density of defect states, as  $\alpha$  follows a Tauc relation with  $p = 2$ , a characteristic of an indirect bandgap. Therefore,  $\alpha$  increases with increasing In concentration due to variation in the bonding arrangements and hence in the defect states.

The dispersion of the refractive index was evaluated using the Wemple-DiDomenico single oscillator model.<sup>23</sup> Wemple and DiDomenico proposed that

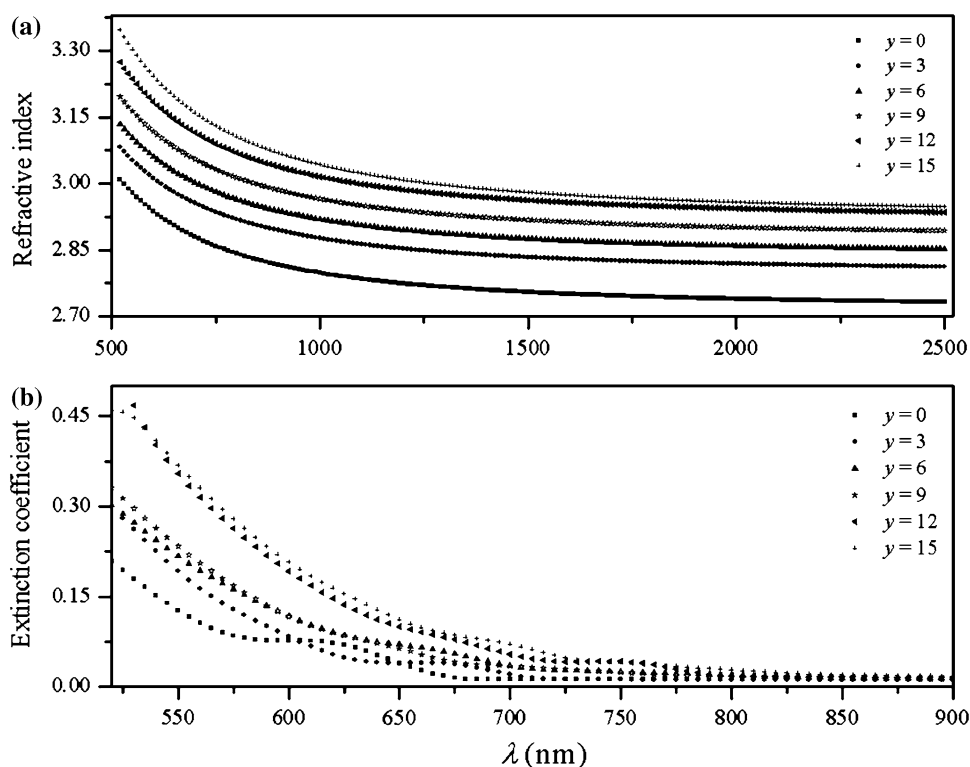


Fig. 2. Variation of (a) refractive index and (b) extinction coefficient with  $\lambda$  for  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  thin films.

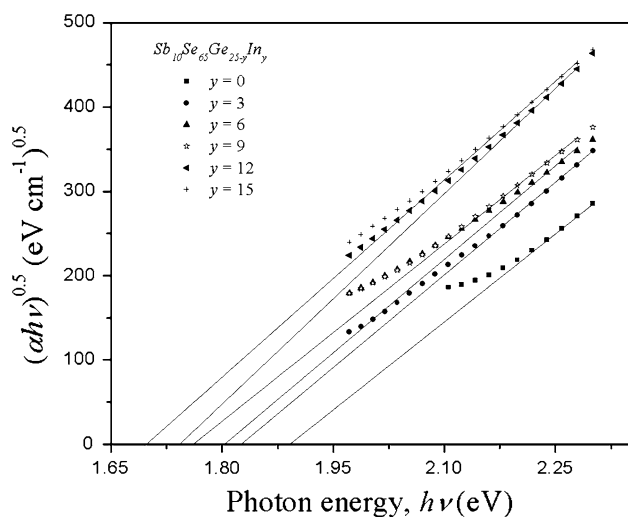


Fig. 3.  $(\alpha h\nu)^{0.5}$  versus  $h\nu$  for  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  thin films.

the energy dependence of the refractive index of a material can be fit to the dispersion relation<sup>23</sup>

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

where  $E_0$  is the oscillator energy and  $E_d$  is the oscillator strength.  $E_0$  and  $E_d$  were determined from the intercept  $E_0/E_d$  and slope  $(E_0 E_d)^{-1}$ , respectively, of the straight fits in Fig. 4. The deviation from linearity is a result of the proximity of the band edge

to the Fermi level at higher photon energies.<sup>24</sup>  $E_0$  is the average energy gap and approximately scales with the Tauc gap, i.e.,  $E_0 \approx 2 E_g^{\text{opt}}$ .<sup>25</sup> Therefore,  $E_0$  also decreases with increasing In alloying concentration (Table I). The static refractive index ( $n_0$ ), i.e., the refractive index when  $h\nu \rightarrow 0$ , was also calculated using Eq. (3). The value of  $n_0$  increases due to the formation of more polarizable In–Se bonds in the system.

To obtain the high-frequency dielectric constant ( $\epsilon_\infty$ ) and  $N/m^*$ , where  $N$  is the free charge carrier concentration and  $m^*$  is the effective mass of the electron,  $n^2$  is plotted against  $\lambda^2$  in Fig. 5, according to the relation<sup>26</sup>

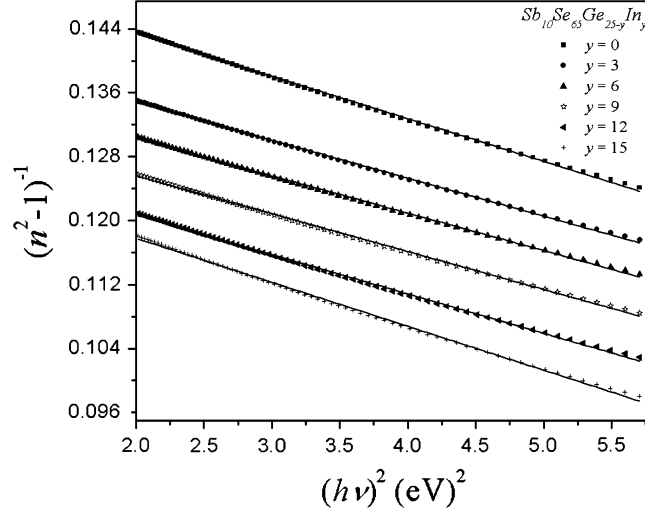
$$n^2 = \epsilon_\infty - B\lambda^2 \quad (4)$$

Here  $B$  is given by  $(e^2 N / 4\pi^2 \epsilon_0 m^* c^2)$ ,  $e$  being the charge of the electron,  $\epsilon_0$  the permittivity of free space, and  $c$  the velocity of light. The dependence of  $n^2$  on  $\lambda^2$  is linear for longer wavelengths. Extrapolating the linear part to  $\lambda = 0$  gives the values of  $\epsilon_\infty$  and  $N/m^*$ . Both  $\epsilon_\infty$  and  $N/m^*$  increase with increasing In concentration (Table I).  $N/m^*$  is directly related to the defect states. Therefore, an increase in  $N/m^*$  signifies an increase in defect states, which is further responsible for the decrease in  $E_g^{\text{opt}}$ .

To assess the nonlinear optical properties of the Sb–Se–Ge–In system, two models, as proposed by Tichy and Ticha<sup>17</sup> and Fournier and Snitzer,<sup>18</sup> were used. Third-order nonlinear susceptibility [ $\chi^{(3)}$ ] is

**Table I. Values of  $E_g^{\text{opt}}$ ,  $E_0$ ,  $E_d$ ,  $n_0$ ,  $\varepsilon_\infty$ ,  $N/m^*$ ,  $n_2$ ,<sup>17</sup> and  $N^*$  for  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  thin films**

$y$	$E_g^{\text{opt}}$ (eV)	$E_0$ (eV)	$E_d$	$n_0$	$\varepsilon_\infty$	$N/m^* \times 10^{55}$ ( $\text{m}^{-3} \text{kg}^{-1}$ )	$n_2 \times 10^{-10}$ (esu) <sup>17</sup>	$N^* \times 10^{22}$ ( $\text{cm}^{-3}$ )
0	1.89	5.66	37.28	2.75	7.61	3.64	1.74	3.77
3	1.83	5.51	38.20	2.82	8.07	3.79	2.13	3.76
6	1.81	5.47	39.16	2.86	8.33	3.98	2.39	3.74
9	1.77	5.34	39.57	2.90	8.59	4.77	2.68	3.73
12	1.75	5.15	39.42	2.94	8.84	5.20	2.99	3.72
15	1.70	4.84	37.57	2.96	9.01	5.83	3.16	3.70

Fig. 4. Plot of  $(n^2 - 1)^{-1}$  versus  $(h\nu)^2$  for  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  thin films.

produced by excitation in the transparent frequency region well below  $E_g^{\text{opt}}$ . According to Miller's generalized rule,  $\chi^{(3)} = A[\chi^{(1)}]^4$ , where  $A = 1.70 \times 10^{-10}$  [when  $\chi^{(3)}$  is measured in esu] and  $\chi^{(1)}$  is the linear optical susceptibility, which for the case of chalcogenide glasses is  $\chi^{(1)} = (n^2 - 1)/4\pi$ .<sup>17</sup> Then, for  $h\nu \rightarrow 0$ ,

$$\chi^{(3)} = \frac{A}{(4\pi)^4} (n_0^2 - 1)^4 \quad (5)$$

The value of  $\chi^{(3)}$  increases monotonically with decreasing  $E_g^{\text{opt}}$  as the In concentration increases (Fig. 6). The value of the nonlinear refractive index ( $n_2$ ) is related to  $\chi^{(3)}$  as<sup>17</sup>

$$n_2 = \frac{12\pi\chi^{(3)}}{n_0} \quad (6)$$

The values of the nonlinear refractive index (in esu) (Table I) were found to increase with the In concentration.

Fournier and Snitzer proposed a relation to calculate the value of  $n_2$  as<sup>18</sup>

$$n_2 = \frac{(n^2 + 2)^2 (n^2 - 1)}{48\pi n N^*} \frac{E_d}{(E_0)^2} \quad (7)$$

where  $N^*$  is the density of polarizable constituents (Table I). The variation of  $n_2$  with normalized photon energy ( $h\nu/E_g^{\text{opt}}$ ) at 800 nm is shown in Fig. 7. The increase in  $n_2$  can be correlated to  $E_g^{\text{opt}}$  by the relation  $n_2 \propto 1/(E_g^{\text{opt}})^4$ ,<sup>27</sup> according to which  $n_2$  increases as  $E_g^{\text{opt}}$  decreases with In addition. This shows the results to be consistent with the given relation. Similar behavior for  $n_2$  has been observed for other materials such as pure silica ( $8.1 \pm 1.2 \times 10^{-14}$  esu),<sup>28</sup>  $[(\text{As}_2\text{Se}_3)_{90}\text{Ge}_{10}]_{95}\text{Bi}_5$  ( $7.06 \times 10^{-11}$  esu),<sup>29</sup> and  $\text{As}_2\text{S}_3$  ( $3.51 \times 10^{-11}$  esu)<sup>30</sup> at 800 nm. These results clearly indicate that the values of  $n_2$  calculated for  $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$  are higher in comparison with reported values.<sup>28-30</sup> Glasses with high  $n_2$  values need moderate laser pulses to change their refractive index.<sup>31</sup> Therefore, the present In-added glassy alloys may be explored for application in fast optical switching devices. Moreover, these high- $n_2$  materials, exploiting third-order electronic polarization, may have short response time and compact fiber design, which may further boost their application in high-speed signal communication.<sup>3</sup>

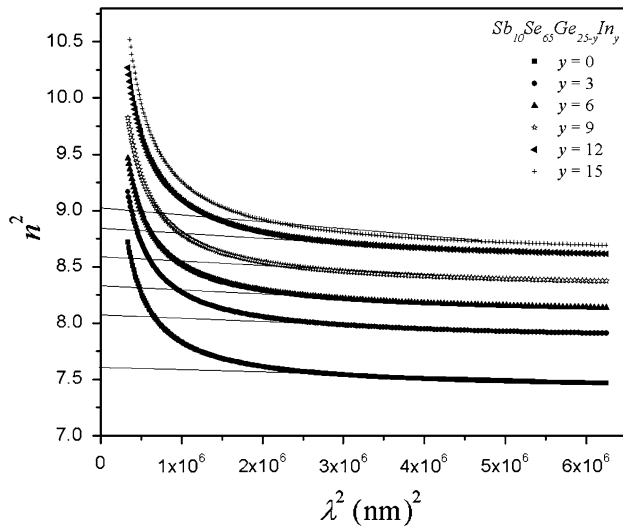


Fig. 5. Plot of  $n^2$  versus  $\lambda^2$  for  $Sb_{10}Se_{65}Ge_{25-y}In_y$  thin films.

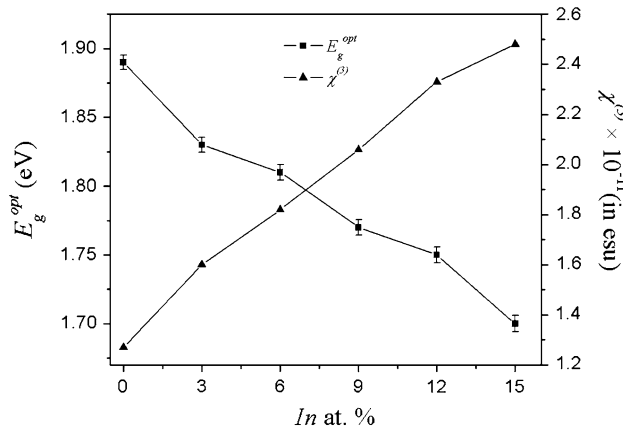


Fig. 6. Composition dependence of  $E_g^{opt}$  and  $\chi^{(3)}$  for  $Sb_{10}Se_{65}Ge_{25-y}In_y$  thin films.

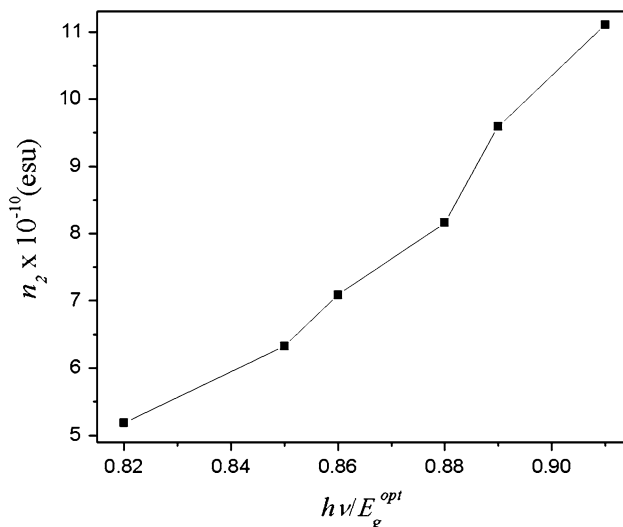


Fig. 7. Variation of  $n_2$  with  $h\nu/E_g^{opt}$  for  $Sb_{10}Se_{65}Ge_{25-y}In_y$  thin films.

### CONCLUSIONS

A red-shift in the transmission spectrum on replacing Ge with In in  $Sb_{10}Se_{65}Ge_{25-y}In_y$  has been observed. The linear refractive index increases due to the formation of more polarizable In–Se bonds. The optical bandgap decreases from 1.89 eV to 1.70 eV on In addition due to the formation of unsaturated Se–Se bonds, which increase the defect concentration and hence the localized states in the system. An increase in localized states has also been confirmed by an increase in  $N/m^*$  values. The static refractive index increases from 2.75 to 2.96. The nonlinear refractive indices increase with In addition and are found to be on the order of  $10^{-10}$  esu.

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