# Effect of bismuth addition on the optical band gap and extinction coefficient of thermally evaporated As-Se-Ge thin films

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Chalcogenide glasses have shown potential application in non-linear optics along with IR applications. In present work, effect of bismuth (Bi) addition on the extinction coefficient (*k*) and optical band gap ( $E_g^{opt}$ ) of $(As_2Se_3)_{90}Ge_{10}$ thin films has been investigated. A single transmission spectrum has been used for the determination of *k* and $E_g^{opt}$. The $E_g^{opt}$ decreases while *k* increases with Bi addition. Results have been explained on the basis of change in density of states at band gap edges and localized states.

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*Keywords:* Chalcogenide glasses, Extinction coefficient, Optical band gap

## 1. Introduction

Chalcogenide glasses are the promising materials for various applications based on their potential properties [1]. Among Chalcogenide glasses, glasses of As-Se-Ge were reported the best because of the fact that As, Ge and Se lies in same period of groups IV–VI and brings the covalent character of the interaction between their atoms thereby increasing the stability [2-5]. Various researchers have studied the electrical, optical and thermal properties of As-Se-Ge system [6-8]. Addition of fourth element Cd, Pb and Sn to As-Se-Ge system has shown remarkable variations in optical band gap and extinction coefficient [9-11].

Generally chalcogenides are p-type semiconductors and the transition from $p \rightarrow n$ has been observed in Ge-Ch-Bi (Ch = S, Se, Te) at higher Bi content [12]. In As-Se-Ge system the addition of Bi, due to a difference in the values of electronegativity ($\chi$) for Bi ($\chi$ = 2.02) with As ($\chi$ = 2.18), Se ($\chi$ = 2.55) and Ge ($\chi$ = 2.01) atoms, may alter the structure and thereby electrical and optical properties. Sharma *et al* [11] has shown that with Bi addition nonlinear refractive index of As-Se-Ge increases by 2.4 times, while on comparing with pure and doped silica glasses results are 2–3 orders higher. This instigates to investigate the addition of Bi in $(As_2Se_3)_{90}Ge_{10}$ thin films for its optical band gap and extinction coefficient. The optical band gap has been calculated using Tauc's extrapolation method [13] which has been successfully used earlier for various chalcogenide compositions [14-16]. Extinction coefficient and optical band gap results are in correlation with non-linear refractive index.

## 2. Experimental details

Bulk Glasses of $(As_2Se_3)_{90}Ge_{10}$ and $[(As_2Se_3)_{90}Ge_{10}]_{95}Bi_5$, were prepared by the melt quenching technique. Elements (As, Se, Ge and Bi) used were of 99.999% purity (Sigma-Aldrich) and weighed according to their atomic percentages. Weighed elements were sealed in evacuated (at ~ 10−4 Pa) quartz ampoules and were kept inside an electric furnace with rocking arrangement. The temperatures of furnace was increased up to 950 $^0$C at a heating rate of 3–4 $^0$Cmin$^{-1}$ and kept at this highest temperature for 24h. The ampoules were frequently rocked during heating to make the melt homogeneous. The quenching was done in ice-cooled water. Ingots of glasses were obtained by breaking the ampoules. Thin films of bulk glasses were deposited on cleaned glass substrates by vacuum evaporation at ~$10^{-4}$ Pa of base pressure (HINDHIVAC model 12A4D India). Thickness of deposited films has been monitored by DTM-101 and estimated from transmission spectra are 910 nm and 948 nm [11]. The evaporation rate of deposited films was 13.1 Å/s and 13.6 Å/s [11]. To check the amorphous nature of deposited films X-ray diffraction (XRD) spectra were taken. No prominent peak in spectra confirms the amorphous nature of films. The compositions of the evaporated samples have been measured by an electron microprobe analyzer (JEOL 8600 MX) on different spots $(\text{size} \approx 2\,\mu\text{m})$ on the sample. The composition of a $2 \times 2\,\text{cm}^2$ sample is uniform within the measurement accuracy of about ±0.1% for $(As_2Se_3)_{90}Ge_{10}$ and ± 0.5% for $[(As_2Se_3)_{90}Ge_{10}]_{95}Bi_5$. The transmission spectra of the thin films in the spectral range 400 – 1500 nm were obtained using a double beam ultraviolet - visible - near infrared spectrophotometer (Perkin Elmer Lambda-750). All the measurements reported were taken at 300 K.

## 3. Results and discussion

For glassy materials optical absorption study helps to estimate the energy gap. The absorption coefficient, which is a measure of spatial decrease in intensity of a propagating light due to its progressive conversion into different forms of energy, changes rapidly close to the band gap and can be divided into three regions [13]. In present investigation, the absorption coefficient ($\alpha$) has been calculated in high and intermediate absorption region of the transmission spectra [11] and not in the weak absorption region. The absorption coefficient ($\alpha$) of deposited thin films can be calculated using the well-known relation [17]

$$\exp(-\alpha d) = T \tag{1}$$

where $d$ is the thickness of the film and $T$ is the transmittance. Fig. 1 shows that the values of absorption coefficient lying in the range of $10^3$ to $10^4$ $cm^{-1}$. The extinction coefficient ($k$), which is a measure of light lost while travelling through the medium, can be calculated using

$$k = \alpha\lambda/4\pi \tag{2}$$

where $\alpha$ is the absorption coefficient calculated from equation (1). Fig. 2 shows the variation of extinction coefficient with wavelength. It has been observed that the value of $k$ decreases with increase of wavelength for the thin films. The extinction coefficient has been observed to increase with the addition of Bi to the system. This might be due to the scattering losses with additional localized states created due to metal impurity in the forbidden gap. The values of $k$ are of the order of $6\times10^{-2}$ with Bi addition confirming the homogeneity and good surface smoothness of the deposited films enhancing the values of non-linear refractive index [11,18,19].

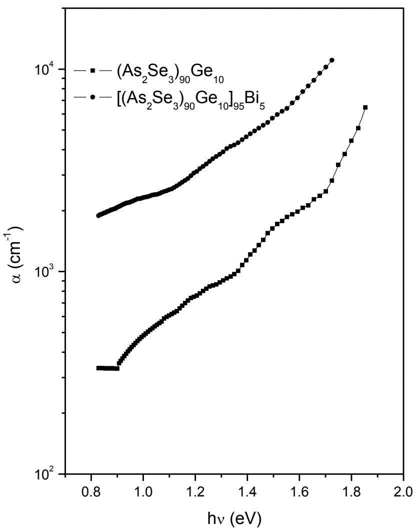


*Fig. 1. Plot of absorption coefficient (α) versus hν for $(As_2Se_3)_{90}Ge_{10}$ and $[(As_2Se_3)_{90}Ge_{10}]_{95}Bi_5$ thin films.*

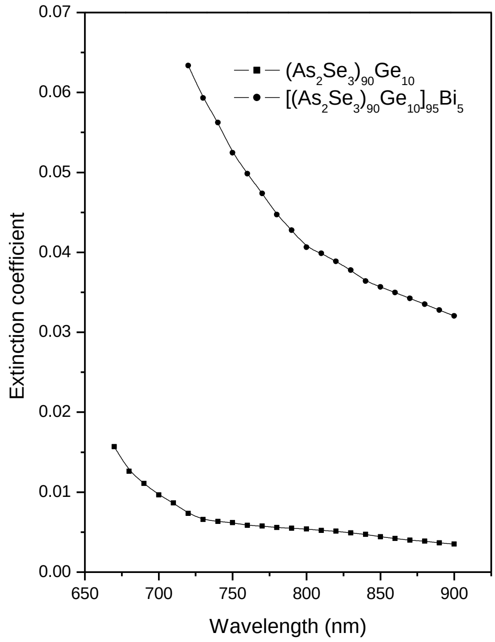


*Fig. 2. Variation of extinction coefficient (k) with wavelength for $(As_2Se_3)_{90}Ge_{10}$ and $[(As_2Se_3)_{90}Ge_{10}]_{95}Bi_5$ thin films.*

The optical band gap ($E_g^{opt}$) has been calculated using the Tauc's relation [13]

$$\alpha h\nu = B(h\nu - E_g^{opt})^2 \tag{3}$$

where $B$ is band tailing parameter attributed to homopolar bonds in the system. Fig. 3 shows a linear graph between $(\alpha h\nu)^{1/2}$ and $h\nu$ confirming the indirect nature of the transitions. The optical band gap values have been estimated by taking the intercept of the extrapolations to zero absorption with photon energy axis. The optical band gap has been found to decrease with the addition of Bi from 1.46 eV to 1.12 eV with ± 0.01 eV. Since in the fundamental absorption region, the absorption is due to the transition from the top of valence band to the bottom of the conduction band. Addition of bismuth may cause an increase in the density of states in the valence band and may also create localized states in the band gap [20]. A shift in the absorption edge will occur towards lower photon energy and consequently a decrease in $E_g^{opt}$ can be explained with an increased tailing [21] in the conduction band edge into the forbidden gap due to the addition of metal impurities. Comparing the optical band gap with nonlinear refractive index values [11] we found that with decreasing optical band gap nonlinear refractive index increases. These results are in good agreement with earlier reported [18,19].

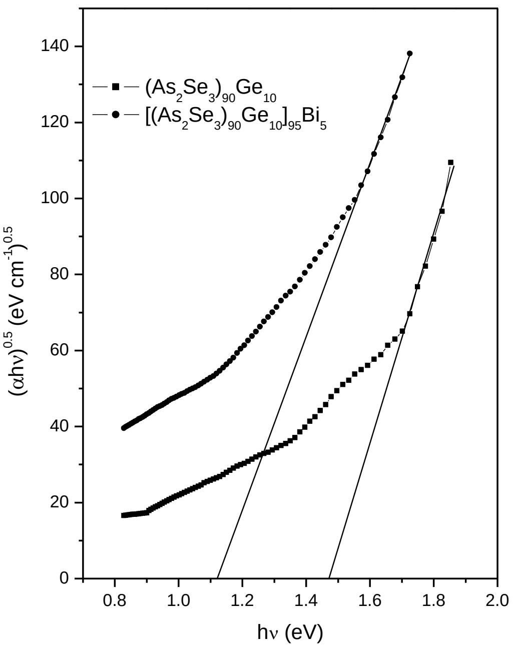


*Fig. 3. Tauc's extrapolation plot for $(As_2Se_3)_{90}Ge_{10}$ and $[(As_2Se_3)_{90}Ge_{10}]_{95}Bi_5$ thin films.*

## 4. Conclusion

Absorption coefficient for $(As_2Se_3)_{90}Ge_{10}$ and $[(As_2Se_3)_{90}Ge_{10}]_{95}Bi_5$ has been found to be in the range of $10^3$ to $10^4$ cm$^{-1}$. The value of extinction coefficient with Bi addition has been found to increase but its value of the order of $10^{-2}$ confirms the homogeneity of deposited films. The optical band gap decreases with the Bi addition. Bi addition lowers the optical band gap and increases the extinction coefficient lead to an increase in non- linear refractive index. Hence the investigated composition with Bi as additive is suitable for non-linear optics.

## References

[1] M. Popescu, J. Optoelectron. Adv. Mater. **7**(4), 2189 (2005).
[2] P. Sharma, S. C. Katyal, J. Phys. D: Appl. Phys. **40**, 2115 (2007).
[3] P. Sharma, S. C. Katyal, Res. Lett. Mater. Sci. 2008, Article ID 826402 (2008).
[4] V. K. Tikhomirov, D. Furniss, A. B. Seddon, J. A. Savage, P. D. Mason, D. A. Orchard, K. L. Lewis, Infra. Phys. Technol. **45**, 115 (2004).
[5] M. F. Churbanov, I. V. Scripachev, V. S. Shiryaev, V. G. Plotnichenko, S. V. Smetanin, E. B. Kryukova, Yu. N. Pyrkov, B. I. Galagan, J. Non-Cryst. Solids **326-327**, 301 (2003).
[6] P. C. Anderson, A. K. Varshneya, J. Non-Cryst. Solids **168**, 125 (1994).
[7] M. F. Churbanov, J. Non-Cryst. Solids, **184**, 25 (1995).
[8] S. Sen, B. G. Aitken, Phys. Rev. B **66**, 134204 (2002).
[9] P. Sharma, S. C. Katyal, Mater. Chem. Phys. **112**, 892 (2008).
[10] P. Sharma, S. C. Katyal, Appl. Phys. B 95, 367 (2009).
[11] P. Sharma, S. C. Katyal, J. Appl. Phys. 107, 113527 (2010).
[12] M. M. EL-Samanoudy, Thin Solid Films 423, 201 (2003).
[13] D. L. Wood, J. Tauc, Phys. Rev. B **5**(8), 3144 (1972).
[14] P. Sharma, S. C. Katyal, Thin Solid Films **515**, 7966 (2007).
[15] N. Sharma, S. Sharda, V. Sharma, P. Sharma, Mater. Chem. Phys. (2012), doi: 10.1016/j.matchemphys.2012.08.034.
[16] P. Sharma, V. S. Rangra, P. Sharma, S. C. Katyal, J. Phys. D: Appl. Phys. **41**, 225307 (2008).
[17] P. Sharma, S. C. Katyal, Mater. Lett. 61, 4516 (2007).
[18] H. Ticha, L. Tichy, J. Optoelectron. Adv. Mater. **4**(2), 381 (2002).
[19] F. Smektala, C. Quemard, L. Leneindre, J. Lucas, A. Barthelemy, C. De Angelis, J. Non-Cryst. Solids **239**, 139 (1998).
[20] N. Barreau, S. Marsillac, J. C. Bernede, T. Ben Nasrallah, S. Belgacem, Phys. Stat. Sol. (a) **184**, 179 (2001).
[21] P. Nagels, L. Tichy, A. Tiska, H. Ticha, J. Non-Cryst. Solids **59–60**, 1015 (1983).

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