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# LASER IRRADIATION EFFECT ON THE OPTICAL PROPERTIES OF a-$Se_{88}Te_{12-x}Al_x$ THIN FILMS

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Thin films of *a*-$Se_{88}Te_{12-x}Al_{-x}$(x= 0,5,10) have been deposited by physical vapour condensation method. Optical properties of as-prepared thin films of *a*-$Se_{88}Te_{12-x}Al_{-x}$and laser irradiated thin films have been studied. These thin films contain nanoparticles of average diameter 50 nm as observed by Scanning Electron Microscopy (SEM). After laser irradiation, the particle size increases which has been verified by SEM investigations. XRD patterns suggest the amorphous nature of as-prepared thin films. In case of laser irradiated samples, the structure changes from amorphous to polycrystalline with presence of significant peaks in XRD patterns of *a*-$Se_{88}Te_7Al_5$&*a*-$Se_{88}Te_2Al_{10}$ have been observed.As-prepared thin films as well as laser irradiated thin films show a decrease in optical band gap with the increase in Al concentration. The optical band gap also decreases after laser irradiation. The optical constants (refractive index (n) & extinction coefficient (k)) have also been calculated and the variation with photon energy and metal (Al) concentration has been studied.

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*Keywords:* Thin films, Optical band gap, Amorphous, Nanoparticles, Optical constants.

## 1. Introduction

Amorphous materials are known for the years as the glasses used for decorative purposes. It was B. T, Kolomiets, who explained the semiconducting behaviour of the glasses having large composition of chalcogen element (S, Se, Te ). Presently, these materials have gained much popularity due to their interesting physical and chemical properties. Many electrical and optical parameters of these glassy materials can be easily tuned by incorporation of III and V groups. The most important application of amorphous semiconductor is in the field of xerography. The use of these materials as an electrochemical sensor is also worth mentioning. Many optical properties of these materials are common with the classical semiconductor. There optical absorbance spectra show a threshold, below the threshold frequency, the light can pass through without loses, while above the threshold frequency the light strongly absorb. It is expected that the development of nano-chalcogenides will lead to the discovery of new materials showing interesting properties to meet out the demands of 21$^{st}$ century. From the discovery of fluorine, CNT, graphene, there are studies discussing the fundamental and technological importance of novel nanostructured materials [1-4]. The quantum confinement in nanoscale materials is most important, which is due to the change in the atomic structure.

To explore the new direction in chalcogenides materials, nano-chalcogenides have been thought to be a better option. These nano-chalcogenides have attracted a lot of attention from the researcher and engineers worldwide for the last few years and are viewed as a large group of interesting materials in which an unusual chemical phenomena are reviewed and as the materials, it open a new direction in science and technology. The optical properties of nano-scale chalcogenides are strongly depend on the size, shape, and surface characteristics. Therefore, much

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attention has been paid to control the parameter to manipulate the optical properties of nano-chalcogenides [5-8]. In the present work, Se is chosen due to its commercial importance in the various field such as photo-element metal coating, solar technology, lubricant, and pharmaceuticals. Te is used as additive materials with Se. Among the various chalcogenides studied so far,the alloys based on Se-Te are the most studied due to higher photo-resistivity [9-11]. Aluminium (Al) is added as a dopant in SeTe system in the present study due to its low density, high strength, superior malleability, excellent corrosion resistance and good thermal and electrical conductivity. The introduction of III element in the as-prepared alloy may result in the creation of ion-covalent bonds. The dopant also affects the lattice perfection and the energy gap of the materials, which is important for the fabrication of the devices. The present work focuses on the optical properties of *a*-$Se_{88}Te_{12-x}Al_{-x}$thin films.

## 2. Experimental details

This research work involved the use of melt quenching technique for the synthesis of bulk samples of *a*-$Se_{88}Te_{12-x}Al_{-x}$(x= 0, 5, 10). The synthesis of this alloy involved the incorporation of high purity materials (Se, Te & Al) (99.999%) purchased from Sigma Aldrich (USA). Initially, the desired atomic percentages of the materials were weighed using a digital microbalance. The alloys of *a*-$Se_{88}Te_{12-x}Al_{-x}$(x = 0, 5 & 10) were prepared by using the desired amount of Se, Te and Al. They were grinded and mixed by using pestle and mortar. The homogeneous powder containing all the materials was kept in quartz ampoules, which were sealed by using a welding torch under a vacuum of $10^{-5}$ Torr. After sealing, these ampoules were inserted into a programmable muffle furnace for rocking and a temperature of $600^0$C was maintained for 10-12 hours. The heating rate was maintained at $10^0$C/min during the increase of temperature. After attaining the set temperature, the ampoules were agitated frequently in order to make a homogeneous alloy. After this process, the ampoules were inserted in to the ice water for quenching the melt. Finally, the ampoules were broken to take bulk pallets out and these pallets were grinded to make them in the form of fine powder.

Thin films of *a*-$Se_{88}Te_{12-x}Al_{-x}$(x = 0, 5 & 10) were prepared by using physical vapour condensation system onto a glass substrate maintained at room temperature. After maintaining the chamber pressure of the order of $10^{-5}$ Torr, an ambient Argon gas was purged into the chamber and ambient gas pressure of 5 Torr was maintained throughout the deposition process of the thin films. The film thickness was measured with the help of a thickness monitor (Edward model FTM7) and the films of thickness of about 20nm were deposited for the present study. To study the effect of laser irradiation He-Ne (6328 $A^0$)laser was used. Thin films were irradiated with He-Ne laser for 5 mins. For measuring the optical absorbance as a function of wavelength, a double beam, UV/VIS/NIR spectrophotometer (Hitachi U3400) was used. X-ray diffractogram (Rigaku model Ultima IV) was used to record the X ray diffraction patterns of as prepared thin films. Scanning electron microscope images of the thin film were recorded by using Scanning Electron Microscope (Carl Zeiss).

## 3. Results and discussion

The morphology of *a*-$Se_{88}Te_{12-x}Al_{-x}$ (x = 0, 5 & 10) thin films has been investigated using Scanning Electron Microscope (Carl Zeiss). Figs.1& 2 show the SEM images of as-prepared and laser irradiated*a*-$Se_{88}Te_7Al_{-5}$thin films. It is revealed that the as prepared thin films contain the nanoparticles, whose diameter ranges from 30-100 nm (Fig. 1). Some of these nanoparticles are aggregated and appear as clusters of average size of150 nm. In case of laser irradiated samples, SEM investigation suggests that the diameter of the particles increases and the size of these particles varies from 100-300 nm (Fig. 2). The composition of as prepared *a*-$Se_{88}Te_7Al_{-5}$thin film has been recorded by EDS technique (EDAX, Ametec.). Fig. 3 presents the EDS results of *a*-$Se_{88}Te_7Al_{-5}$thin film. On the basis of EDS results, it is verified that Se, Te and Al are present in as-prepared thin film with almost same composition.

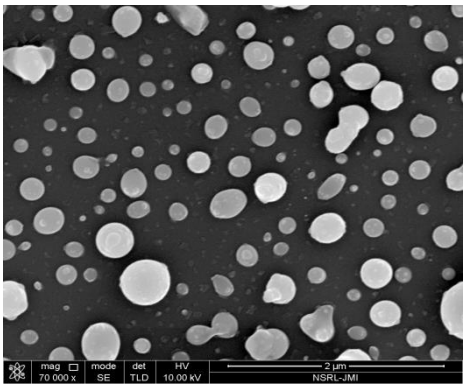


*Fig. 1. SEM Images of as-prepared a-$Se_{88}Te_7Al_{-5}$ thin films.*

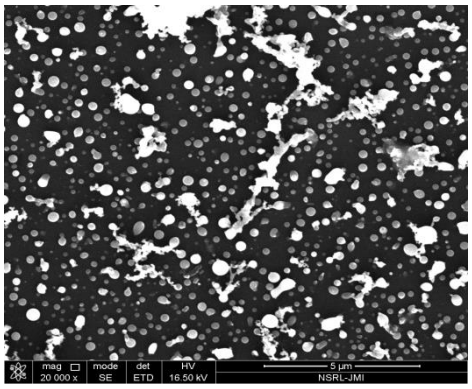


*Fig. 2. SEM Images of laser irradiated a-$Se_{88}Te_7Al_{-5}$ thin films.*

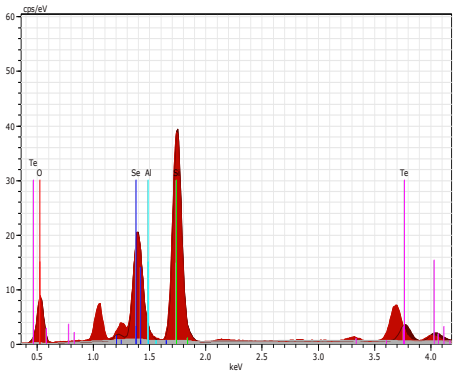


*Fig. 3. EDS spectrum of a-$Se_{88}Te_7Al_{-5}$ thin films.*

XRD patterns of the as-prepared thin films of *a*-$Se_{88}Te_{12-x}Al_{-x}$and laser irradiated thin films have been recorded by using a Rigaku Ultima IV diffractometer [copper target was used as the source with $\lambda = 1.54056A^o$ (Cukα1)]. The range of scanning is set from $20^o - 85^0$ at the rate of $2^0$/min. The XRD patterns of theses samples are shown in the Fig.4&5. We have not observed any significant peak in XRD pattern of as-prepared thin films, which suggest the amorphous nature of as-prepared thin films. XRD spectra of laser irradiated thin films suggest polycrystalline nature. The crystallinity of laser irradiated thin films increases with the increase in metal (Al) concentration.

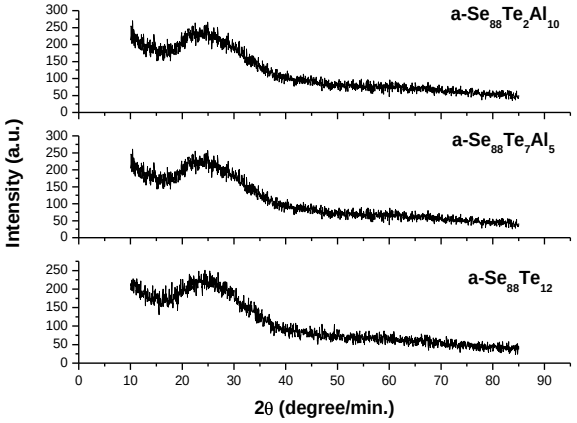


*Fig. 4.X-ray diffraction pattern of as-prepared a-$Se_{88}Te_{12-x}Al_{-x}$ thin films.*

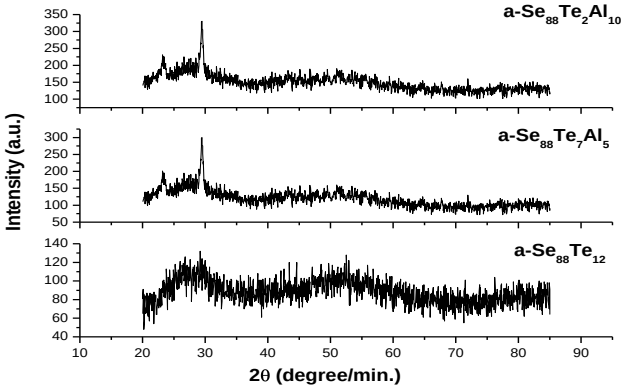


*Fig. 5. X-ray diffraction pattern of $Se_{88}Te_{12-x}Al_{-x}$ thin films after laser irradiation.*

Optical properties of *a*-$Se_{88}Te_{12-x}Al_{-x}$(x = 0, 5 & 10) thin films composed of nanoparticles have been studied at room temperature and a wavelength range of 400-900nm was chosen for recording the optical absorption and reflection spectra. The optical density recorded using UV-Vis spectrophotometer can be converted in to absorption coefficient (α) using the relation [12-13].

$$\alpha = \text{Optical Density/ Film Thickness} \quad (1)$$

To calculate the optical band gap of a material, we use the following relation

$$(\alpha h\nu)^{1/n} = B\,(h\nu - E_g) \quad (2)$$

where, ν is the frequency of the incident beam, B is a constant, $E_g$ is the optical band gap and n is an exponent. The values of n can be taken as 1/2, 3/2, 2 & 3 for different electronic transitions responsible for absorption [14-15]. The present system of Se-Te-Al nanoparticles follows the rule of direct transition at the extremum, lyings at the same point of k space [5]. On the basis of direct transition, equation (2) is rewritten as given below [6-7].

$$(\alpha h\nu)^2 \propto (h\nu - Eg) \quad (3)$$

The dependence of $(\alpha h\nu)^2$ with photon energy (hν) for as-prepared *a*-$Se_{88}Te_{12-x}Al_{-x}$thin films and laser irradiated thin films is presented in Fig. 6&7 The value of energy gap has been calculated by taking the X-axis intercept of the plot $(\alpha h\nu)^2$ Vs hν. The calculated values of $E_g$ are

given in Table 1. Khan et al [16] reported the laser induced amorphization and crystallization on $Se_{80}Te_{20-x}Sb_{-x}$thin films. They observed that the change in the optical band gap due to crystallization and amorphization. They attributed this change in the optical band gap to the increase in the grain size and the reduction inthe disorder of the system. Khan et al [17] fabricated as-prepared $Se_{75}S_{25-x}Cd_x$ chalcogenide thin films and performed thermal annealing of thin films. They reported the variation of optical constants (absorption coefficient, refractive index and extinction coefficient) as a function of photon energy in the wavelength region 400–1000nm. An increase in absorption coefficient and optical band gap was observed with the increase in annealing temperatures. The same trend was observed for refractive index (n) and the extinction coefficient (k) with increasing annealing temperature. Bahishti et al [18] reported the effect of laser irradiation on the optical properties of $Se_{96-x}Te_4Ga_x$ thin films. They reported an increase in optical band gap in as-prepared thin films as well as laser irradiated thin films with the incorporation Ga. The optical band gap decreased after laser irrdation. Al-Hazmi [19] reported the optical properties induced by laser irradiation in the thin films of $Se_{75}S_{15}Ag_{10}$. They observed that the absorption coefficient and optical band gap increased where as a decrease in the value of refractive index and extinction coefficient was observed with the increase in laser irradiation time. They interpreted results with the help of change in the concentration of localized states due to shift in Femi level. In the present work, we observe a decrease in the value of optical band gap with the increase in Al content for the sample without laser irradiation. The estimated values of optical gap of laser irradiated thin films irradiated also show the same trend. The increase in the particle size/the density of defect states may be suggested to be responsible for the reduction in band gap due to increase in metal (Al) content/ laser irradiation. The value of optical band gap also reduces after laser irradiation, which suggests that the particle size increase on laser irradiation.

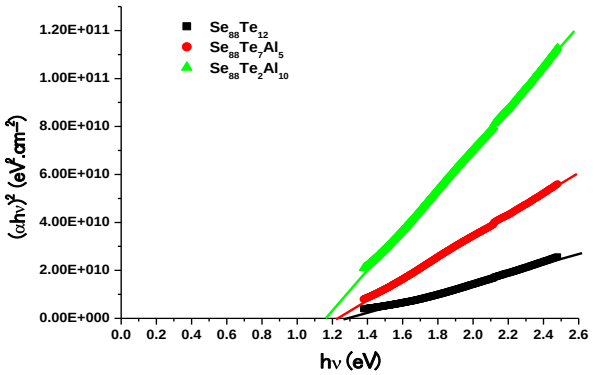


*Fig. 6. $(\alpha h\nu)^2$ against photon energy $(h\nu)$ in a-$Se_{88}Te_{12-x}Al_{-x}$ thin films.*

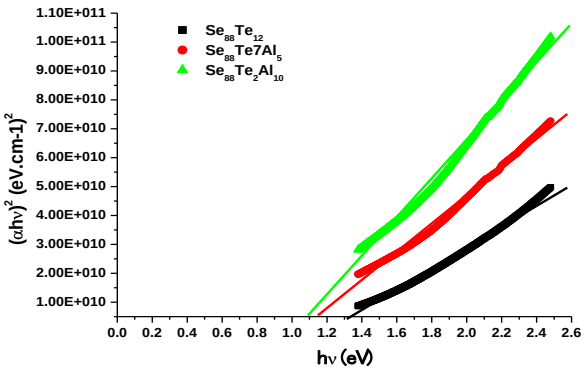


*Fig. 7. Variation of extinction coefficient (k) with incident photon energy $(h\nu)$ in a-$Se_{88}Te_{12-x}Al_{-x}$ thin films.*

Using the model proposed by Mott and Davis, this decrease in the value of optical band gap with the increase in Al content in the thin film of *a*-$Se_{88}Te_{12-x}Al_{-x}$nanoparticles can be explained [20]. In this system of *a*-$Se_{88}Te_{12-x}Al_{-x}$, the decrease in the optical gap may be due to either change in width of the localized states caused by the presence of defects or unsaturated bonds or the presence of high concentration of localized states in the energy band gap. It may due to shift in Fermi level caused by the increasing concentration of Al and the position of the Fermi level is determined by the distribution of electrons in the localized states [21].

The refractive index (n) and extinction coefficient (k) are the important optical constants for studying the suitability of these nanoparticles for the application in optical disks. We use the popular relation given by equation (4) to calculate the extinction coefficient (k).

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

where, $\lambda$ is the wavelength of the incident light and $\alpha$ is the absorption coefficient.

We employ the well known theory of reflectivity of light to estimate the values of refractive index (n) and extinction coefficient (k). Using this theory, the reflectance of light can be expressed in term of Fresnel's coefficient and the following relation can be used to express the reflectivity on an interface [22-23];

$$R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2] \tag{5}$$

Fig. 8&9 show the dependence of photon energy with the extinction coefficient (k) for as-prepared *a*-$Se_{88}Te_{12-x}Al_{-x}$thin films composed of nanoparticles and laser irradiated thin films. In the both the cases, the value of extinction coefficient increases with the increase in photon energy. The dependence refractive index (n) with the photon energy for as-prepared *a*-$Se_{88}Te_{12-x}Al_{-x}$thin films composed of nanoparticles and laser irradiated thin films is presented in Figs.10&11. Al-Ghamdi et al [24] reported the variation of the optical constants (absorption coefficient (a), refractive index (n), extinction coefficient (k), real and imaginary part of dielectric constant) for a-$Se_{96-x}Te_4Ag_x$ (where x = 0, 4, 8, 12) thin films as a function of photon energy. They reported an increase in the optical band gap and decrease in the values of n and k on adding Ag in Se–Te system. The results were interpreted on the basis of change in concentration of localized states due to the shift in Fermi level. Khan et al [25] prepared the polycrystalline $Se_{85}Te_{10}Pb_5$ and $Se_{80}Te_{10}Pb_{10}$ chalcogenides using ball milling. They reported the formation of nanoparticles of diameter ranging from 5-20 nm. They observed an increase in that the absorption coefficient, optical band gap and extinction coefficient, whereas the refractive index was found to decrease with the increase in milling time. The results were interpreted with help of milling time and size effect. In our case, we have observed an overall decreasing pattern in the value of refractive index with the increase in photon energy. These calculated values of optical constants are presented in Table 1 and these values show close agreement with the results reported by various workers [26-27]. For the as-prepared *a*-$Se_{88}Te_{12-x}Al_{-x}$thin films containing nanoparticles and laser irradiated thin films, the values of refractive index (n) and extinction coefficient (k) decreases with the increase Al content. This decrease the values of refractive index (n) may also be interpreted on the basis of change in concentration of localized states due to the shift in Fermi level. On the basis of above results, it is suggested that the spectral and dopant dependence of optical band gap and optical constants with the photon energy may be helpful to decide the suitability of this system for the application in optical data storage devices.

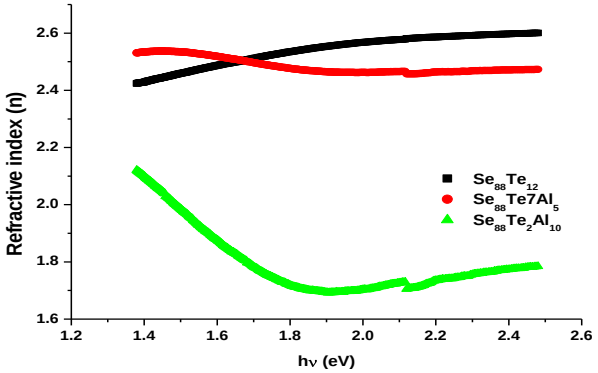


*Fig. 8.Variation of refractive index (n) with incident photon energy (h ν) in a-$Se_{88}Te_{12-x}Al_{-x}$ thin films.*

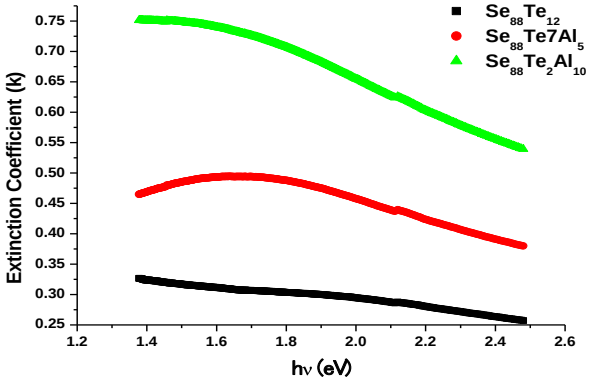


*Fig. 9. $(\alpha h\nu)^2$ against photon energy (h ν) in a-$Se_{88}Te_{12-x}Al_{-x}$ thin films after laser irradiation.*

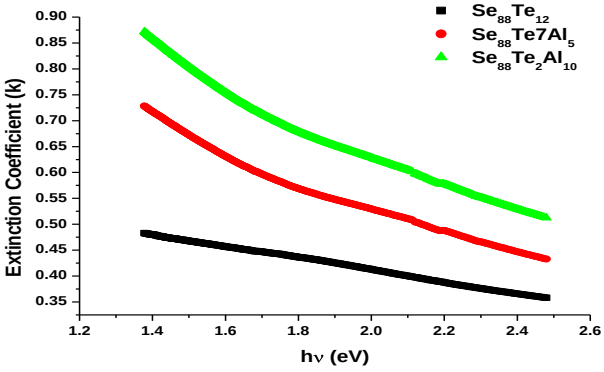


*Fig. 10. Variation of extinction coefficient (k) with incident photon energy (h ν) in a-$Se_{88}Te_{12-x}Al_{-x}$ thin films after laser irradiation.*

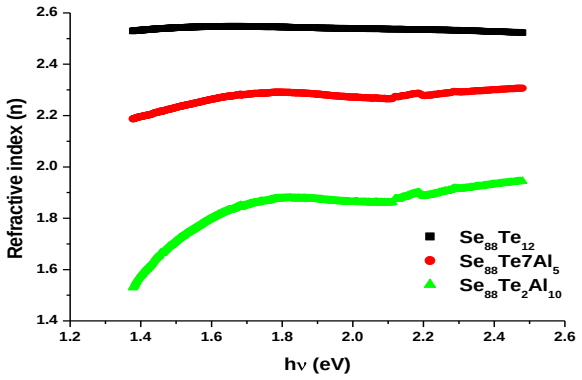


*Fig. 11. Variation of refractive index (n) with incident photon energy (h ν) in a-$Se_{88}Te_{12-x}Al_{-x}$ thin films after laser irradiation.*

*Table-1. Optical parameters in $Se_{88}Te_{12-x}Al_{-x}$ thin films at 600 nm.*

| *Sample* | *$E_g$ (eV)* | α ($cm^{-1}$) | *k* | *n* |
|---|---|---|---|---|
| $Se_{88}Te_{12}$ | *1.27* | *$6.07 \times 10^4$* | *0.2901* | *2.58* |
| $Se_{88}Te_7Al_{-5}$ | *1.22* | *$9.32 \times 10^4$* | *0.4452* | *2.46* |
| $Se_{88}Te_2Al_{-10}$ | *1.15* | *$1.33 \times 10^5$* | *0.6363* | *1.72* |

*Table-2. Optical parameters in $Se_{88}Te_{12-x}Al_{-x}$ thin films at 600 nm after laser irradiation.*

| *Sample* | *$E_g$ (eV)* | α ($cm^{-1}$) | *k* | *n* |
|---|---|---|---|---|
| $Se_{88}Te_{12}$ | *1.34* | *$8.46 \times 10^4$* | *0.4042* | *2.54* |
| $Se_{88}Te_7Al_{-5}$ | *1.14* | *$1.08 \times 10^5$* | *0.5168* | *2.27* |
| $Se_{88}Te_2Al_{-10}$ | *1.08* | *$1.28 \times 10^5$* | *0.6123* | *1.86* |

## 4. Conclusion

Optical properties of *a*-$Se_{88}Te_{12-x}Al_x$thin films composed of nanoparticles have been studied. The optical band gap is found to decrease with the increase in metal content for as-prepared thin films as well as laser irradiated thin films. The extinction coefficient showed an increasing trend with the increase in photon energy, whereas the refractive index showed an overall decrease with increase in photon energy for both the cases. On the basis of calculated values of optical band gap and optical constants and their variation with dopant concentration, it is easy to understand the suitability of the materials for the applications in optical disks.

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## References

[1] Zishan H. Khan, M. Husain, Materials Science Research India **03 (1a).** 1 (2006).
[2] Zishan H. Khan, S. Khan and M. Husain, Current Nanoscience **6,**1 (2010).
[3] Zishan H. Khan, Applied Surface Science (Netherland) **255**,8874 (2009).
[4] Numan Salah, Sami S. Habib, Zishan H. Khan, Najlaa D. Alharbi. J. Luminescence (2013)

(Holland) **143**,640 (2013).
[5] M. A. Alvi and Zishan H. Khan, Nanoscale Research Letters, **8,** 148(2013).
[6] Numan Salah, Sami S. Habib, Adnan Memic, NajlaaD.Alharbi, Saeed S. Babkair, Zishan H. Khan, Thin Solid Films **531**,70 (2013).
[7] Numan Salah, Sami Habib, Zishan H. Khan, and Shamshad A. Khan, J. Nanomater. (USA) (2012).
[8] Zishan H. Khan, A. A. Al-Ghamdi, Shamshad A. Khan, Sami Habib &Numan Salah Nanoscience& Nanotechnology Letters (USA)**3,**1 (2011).
[9] Numan Salah, Sami S Habib**,** Zishan H Khan, Nanoscale Res. Letts. (UK) **7**(1), 509 (2012)
[10] Zishan H. Khan, A. Al-Ghamdi& Faisal A. Al-Agel. Mater. Chem. Phys. **134,**260 (2012).
[11] Zishan H. Khan, Shamshad A. Khan and A. A. Al-Ghamdi, Optics & Laser Tech. (USA) **44** 6 (2012).
[12] Shamshad A. Khan, Zishan H. Khan, A. Sibaee, A. A. Al-Ghamdi, Physica B (Netherland) **405,**3384 (2010).
[13] Zishan H. Khan, Shamshad A. Khan, Numan Salah, Sami Habib, Nanoscale Res. Letters (UK) **5,**1512 (2010).
[14] Zishan H. Khan& M. Husain, Journal of Alloy and Compound (UK) **486,**774 (2009).
[15] Anis Ahmad, S. A. Khan, KirtiSinha, Lokesh Kumar, Zishan H. Khan, M. Zulfeqaur, M. Husain,Vacuum **82**(6),608 (2008).
[16] Shamshad A. Khan, M. Zulfequar, M. Husain, Vacuum **72,**291 (2004).
[17] Shamshad A.Khan, J.K.Lal, A.A.Al-Ghamdi , Optics & Laser Technology **42,**839 (2010).
[18] Adam A. Bahishti, M. A. Majeed Khan, S. Kumar, M. Husain, M. Zulfequar Chalcogenide Letters **4**(12),155 (2007).
[19] F. S. Al-Hazmi, Chalcogenide Letters,**6**(2),63 (2009).
[20] N.F. Mott, E.A. Davis, Electronics Processes in Non-Crystalline Materials, Oxford: Clarendon, (1979) 428.
[21] K. Oe, Y. Toyoshima, J. Non- crystal, solids **58**,304 (1973).
[22] M. Ilyas, M. Zulfequar, Zishan H. Khan and M. Husain, J. Optical Materials (USA) **11**,67 (1998).
[23] Z. H. Khan, M. Zulfequar, M. Husain, Journal of Modern Optics **44**(1), 55 (1997)
[24] A.A. Al-Ghamdi, Vacuum **80**,400 (2006).
[25] Shamshad A. Khan, F.A. Al-Agel, A.A. Al-Ghamdi, Superlattices and Microstructures **47,** 695 (2010).
[26] Shamshad A. Khan, F.S. Al-Hazmi, S. Al-Heniti, A.S. Faidah, A.A. Al-Ghamdi, Current Applied Physics **10**,145 (2010).
[27] M.I. Abd-Elrahman, Rasha M. Khafagy, Shiamaa A. Zaki, M.M. Hafiz, J. Alloys & Compd., **571,** 118 (2013).