

Structural, Morphological and Optical Studies of As-Prepared and Annealed Cadmium Doped $Te_{90-x}Se_{10}Cd_x$ Chalcogenides

¹Arvind Kumar Verma, ¹Susheel Kumar Singh,
¹R. K. Shukla and ²K. C. Dubey

¹Department of Physics, University of Lucknow, Lucknow – 226007, India.

²Department of Physics Shia P. G. College Lucknow – 226020, India.

Email: krishnacdubey@gmail.com

Abstract

The present study is undertaken in order to investigate the influence of addition of cadmium (Cd) with decreasing at.wt. % of Tellurium (Te) at constant at wt% of Selenium (Se) on the optical properties of the $Te_{90-x}Se_{10}Cd_x$ ($x = 0, 10, 20$). Optical Studies of the metal doped chalcogenide prepared by melt quenching method from 99.999% pure elements has been reported. XRD pattern reveals that as-prepared and thermally annealed chalcogenide alloys show polycrystalline nature and a combination of hexagonal and cubic phase. Average crystal size observed by Scherrer's formula for as-prepared and thermally annealed sample S1, S2, S3 of $Te_{90-x}Se_{10}Cd_x$ ($x=0, 10, 20$) are 22.83, 33.86, 29.58 nm and 21.51, 49.27, 46.34 nm respectively. FESEM images of the sample S1, S2, and S3 are uniform which shows the presence of some micro-crystallites of the synthesised material. Spectral dependence of the absorption spectra recorded in the range of 200 – 1000 nm for as-prepared and thermally annealed samples in normal wavelength scanning mode is shown by UV-Visible spectroscopy. Crystal size and optical band gap (E_g) of the as-prepared and thermally annealed sample increases while dislocation density, absorption coefficient of each sample decrease with increasing Cd% in the sample. The luminescence intensity of as-prepared sample S3 (20% of Cd) is much more than its annealed sample at 330 nm excitation wavelength.

Keywords: $Te_{90-x}Se_{10}Cd_x$ ($x = 0, 10, 20$), XRD, FESEM, UV/VIS/NIR, PL.

1. Introduction

The attention in this paper is focused on discussing the optical properties of chalcogenide alloys because any glass is free of defects such as bubbles or imperfections; it can be considered that a glass is a perfect material for light propagation (Bruno, B. et. al, 2009). Chalcogenide glasses are oxygen-free inorganic glasses containing one or more kinds of chalcogen elements (Pandey, V. & Tripathi, S. K. 2006). Te-rich alloys show metallic nature due to semi-metallic nature of Te. It limits the glass forming ability whereas Se-rich alloys show a semiconducting nature (Fainchtein, R. & Thompson, J. C. 1983). Te-rich chalcogenides are poor glass formers but possess very large optical windows. The main difference between Se and Te is the nature of the bonding responsible for the interchain cohesion. Te is beneficial for getting low vibrational modes. However, it is also a risky operation because of the high tendency of Te to produce electron delocalization and bonds prone to generate microcrystals (Bureau, B. et al., 2008). The increase of Te content leads to the formation of composition with a higher degree of disorder as well as higher densities of localised states. Chalcogenide glasses are generally less strong more weakly bonded materials than oxide glasses. The change in the optical properties of the composition may be explained by assuming that Te atoms act

as an impurity centre in the mobility gap (Sharma, P & Katyal, S. C. 2007), (Maan, A. S. & Goyal, D. R. 2008), (Mehra, R. M. et al., 1993). On the other hand, Te based glasses, due to their extreme tendency to crystallise, have found applications as phase change materials for optical storage in the Digital Versatile Disk (DVD) technology (Feinleib, J. et al., 1971), (Yamada, N. O. et al., 1991). These glasses are being studied mostly for applications as passive devices (lenses, windows, fibres) and also attractive for the preparation of active devices such as Laser fibre amplifiers and nonlinear components (Lezal et al., 2004).

In the present work, the effect of Cd additive on the optical properties of $\text{Te}_{90-x}\text{Se}_{10}$ has been studied. The optical parameters; absorption coefficient (α), optical band gap (E_g) of the $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x=0, 10, 20$) alloys have been calculated analysing their absorption spectra.

2. Experiment Setup

In the present work, melt quenching method has been adopted to prepare $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x = 0, 10, 20$) chalcogenide alloys were prepared from 99.999% pure Te, Se, and Cd elements. The exact amount of alloying elements were weighed according to their atomic weight percentages using an electronic balance with the least count of a 10^{-4} gram and then placing into ultra-cleaned quartz ampoules (length ≈ 5 cm and internal diameter ≈ 8 mm). The ampoules were evacuated and sealed under a vacuum of 10^{-3} Torr with an oxygen-indane flame torch using rotary pumps to avoid reaction of alloying elements with oxygen at a higher temperature. The sealed ampoules were heated in a furnace at the rate of $4^\circ\text{C}/\text{min}$. The temperature was raised up to 1000°C and was maintained for 10 hours. During the heating process, the ampoules were constantly rocked by a ceramic rod to ensure the homogeneity of the alloying materials. The ampoules with molten materials were rapidly quenched into the ice-cooled water to allow glass formation and to avoid crystallisation. The ingots of chalcogenide materials were taken out from ampoules by breaking them. The obtained melt was ground into powder form and filtered to obtain homogeneous alloy. Obtained as-prepared sample is further annealed for 4 hours at 250°C fixed temperature to remove internal stress to make the material less brittle.

Characterization of the filtered as-prepared and annealed sample of $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x = 0, 10, 20$) are named as S1 ($\text{Te}_{90}\text{Se}_{10}$), S2 ($\text{Te}_{80}\text{Se}_{10}\text{Cd}_{10}$), and S3 ($\text{Te}_{70}\text{Se}_{10}\text{Cd}_{20}$) respectively was carried out by XRD, FESEM, UV/VIS/NIR spectroscopy and Photoluminescence (PL) spectroscopy. Crystal structures and phase of as-prepared and annealed sample S1, S2, S3 were characterised by X-ray diffraction (XRD) using Ultima IV model from Rigaku, Japan employing $\text{Cu K}\alpha$ radiation (wavelength 1.5404 \AA) in the 2θ range from 20° to 80° with a scan speed of $2^\circ/\text{sec}$. The Surface morphology was studied using the JSM-7610F Model FESEM from JEOL, Japan. The magnification used was $10,000\times$. Optical absorption spectra were recorded using JASCO V670 UV/VIS/NIR spectrophotometer in the spectral range of 200 to 1000 nm using a quartz cuvette with an optical path of 1 cm for all samples dissolved in ethyl alcohol at normal incidence. The room temperature Photoluminescence (PL) spectra of as-prepared and annealed sample were recorded with the help of LS55 Perkin Elmer Fluorescence spectrometer at 330 and 380 nm excitation wavelength respectively.

Results and discussion

2.1. Powder X-Ray Diffraction Analysis

To identify the crystalline phase of the sample, X-ray diffraction was carried out for an as-prepared and thermally annealed sample of $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x=0, 10, 20$) as shown in Fig. 1 which shows that structural peaks diffracted by the crystals of the synthesised sample. The presence of sharp peaks confirms the polycrystalline nature of all as-prepared and annealed samples (Shinde, S. K., et al.,

2014), (Haoyong, Y. et al., 2005). All the samples show polycrystalline phase; it has been reported by various authors that the XRD pattern of Te-rich alloys shows a high degree of crystallinity.

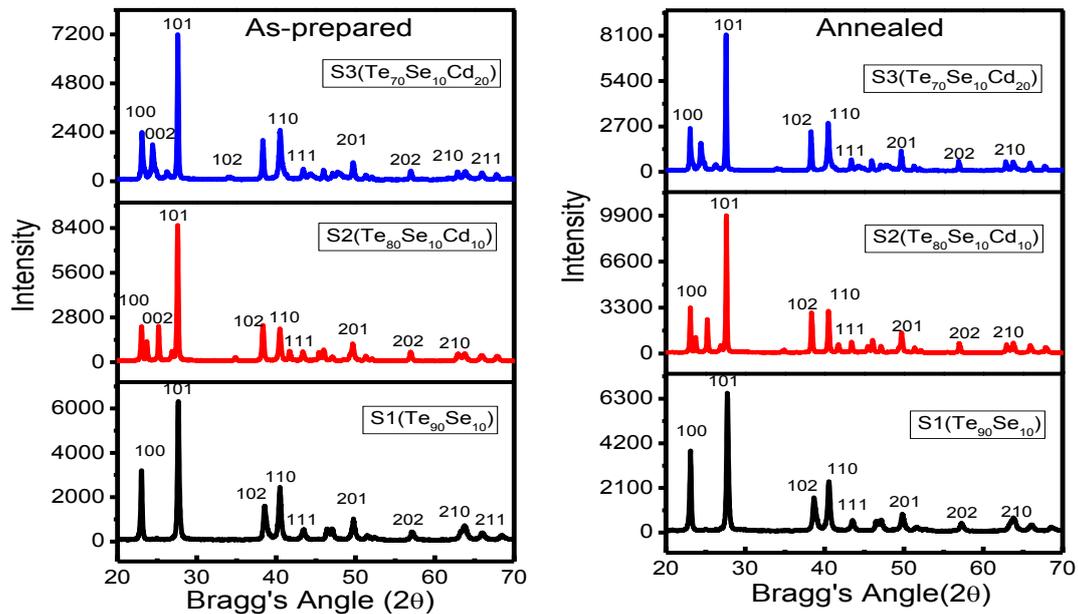


Fig.1. XRD pattern of $Te_{90-x}Se_{10}Cd_x$ for As-prepared and Annealed sample S1, S2, and S3

The peaks observed at (1,0,0), (2,0,1), and (2,1,0) confirms the hexagonal phase and the one observed at 101 confirm the cubic phase of the as-prepared and annealed composition among all the peaks of the sample S1, S2, and S3 as concluded from DB card no. (000040554). The crystallite size D corresponding to observed peaks is calculated using Scherrer's formula ($D = K \lambda / \beta \cos \theta$), where k is constant dependent on crystallite shape ($=0.89$), λ is X-ray wavelength (1.5405 \AA), β is FWHM (full width at half maxima in radian) and θ_B is Bragg angle (Brian & Younan, X., 2002), (Bhattacharya, C. & Datta, J. 2007), (Nasir, Md. & Zulfequar, M., 2012). Using the crystallite size, the rough approximation of a number of defects in the sample is defined by dislocation density (δ) have been calculated using the following formula; $\delta = n/D^2$ Where n is a factor, which equals unity giving minimum dislocation density. The crystallite size D and dislocation density (δ) have been calculated using above formula and values of as-prepared and annealed samples are given in Table.1. As the particle size increases, the dislocation density (defects) of the material decreases. Another author has also observed a similar trend (Mishra, P. K. et al., 2014), (E-Abd El-Wahab, 2000). The crystal size of Cd-doped sample S2(10%) has maximum value with lowest defects in the material with respect to sample S3(20%) and S1(pure) of as-prepared and annealed sample. Reactivity, scattering, and surface area of the material reduce as crystal size of the as-prepared and annealed sample increases.

2.2. Surface morphology

In FESEM, the electrons interact with atoms in the sample, which produces various signals that can be detected. This gives important information regarding growth mechanism, shape, and size of the sample. Fig. 2 shows the Field Emission Scanning Electron Micrographs of the as-prepared and annealed sample; it can be observed that there is not much change in the morphology of the prepared samples with changing Cadmium content for sample S1, S2, and S3. From FESEM micrographs, it is evident that images of the as-prepared and annealed sample S1, S2, and S3 are uniform and without any pinholes or cracks, which shows the presence of some nano and micro-crystallites of the synthesised material.

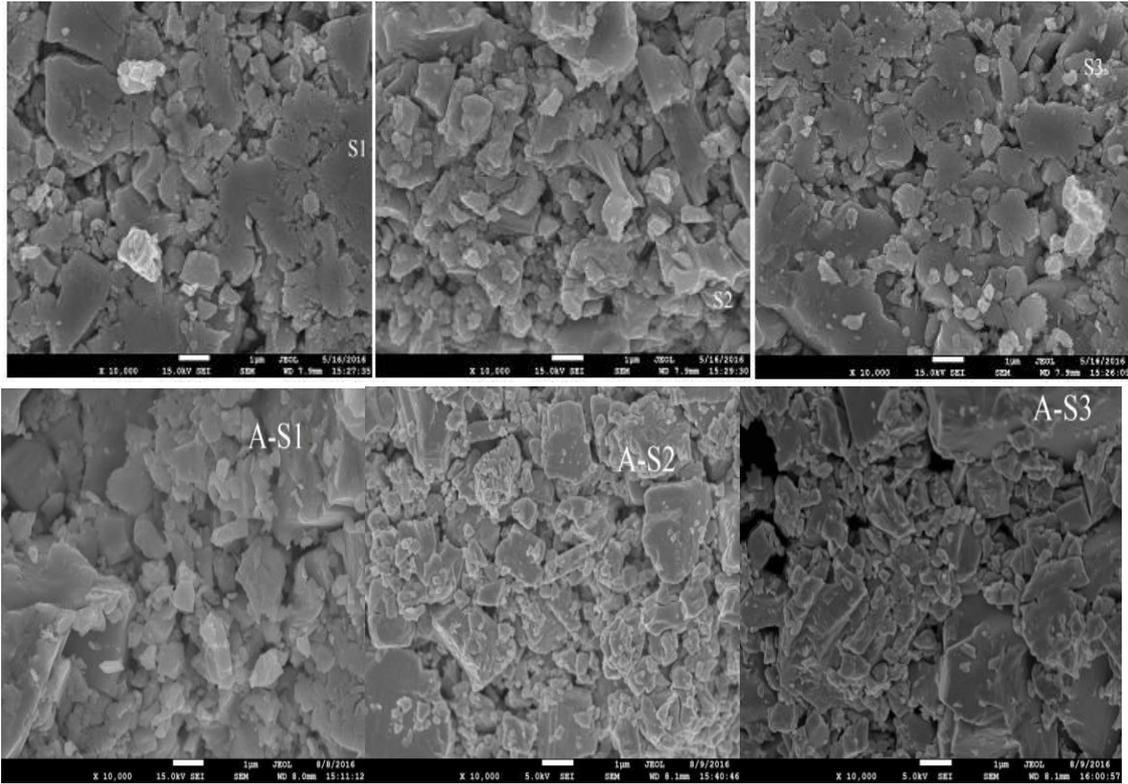


Fig. 2 FESEM images of As-prepared (S1, S2, S3) and Annealed (A-S1, A-S2, A-S3) sample for $Te_{90-x}Se_{10}Cd_x$

Table.1: Shows the Crystal size by XRD and Optical parameters of as-prepared and annealed $Te_{90-x}Se_{10}Cd_x$ ($x = 0, 10, 20$) chalcogenide

Sample	Crystal size (nm) by XRD		Dislocation density in (nm ⁻²)		Absorption coefficient(α) in cm ⁻¹		Optical band gap (Eg) in eV	
	As-prepared	Annealed	As-prepared	Annealed	As-prepared	Annealed	As-prepared	Annealed
S1($Te_{90}Se_{10}$)	22.83	21.51	0.001919	0.002161	66.12 at 4.99 eV	$4.52 \cdot 10^2$ at 1.74 eV	4.28	2.65
S2($Te_{80}Se_{10}Cd_{10}$)	33.86	49.27	0.000872	0.000412	44.32 at 5.00 eV	$1.08 \cdot 10^2$ at 4.61 eV	4.50	2.96
S3($Te_{70}Se_{10}Cd_{20}$)	29.58	46.34	0.001143	0.000466	62.06 at 4.97 eV	$4.77 \cdot 10^1$ at 4.57 eV	4.36	3.23

2.3 Optical Studies

2.3.1 Absorption coefficient

Absorption coefficient (α) is the property of a material which defines the amount of incident light photon absorbed by it which depends upon incident photon energy as well as the composition of the material. Variation of absorption coefficient (α) with photon energy can be explained in term of fundamental absorption, excitation absorption and valence band acceptor absorption (Al-Ghamdi, A.A. 2006). The absorption coefficient (α) has been evaluated by Beer-Lambert law ($\alpha=2.303A/t$), Where A is optical absorption which depends on wavelength and density of point defects and (t) is light path length (10 mm) (Halimah, M.K. & Zainal, A.S. 2010). Fig.3 shows the absorption coefficient of as-prepared and annealed sample S1, S2, S3 for $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x = 0, 10, 20$) with incident photon energy range. The absorption coefficient of the thermally annealed sample has more than that of the as-prepared sample but continuously decreases as the doping concentration of Cd increases with respect to incident photon energy in as-prepared and annealed sample.

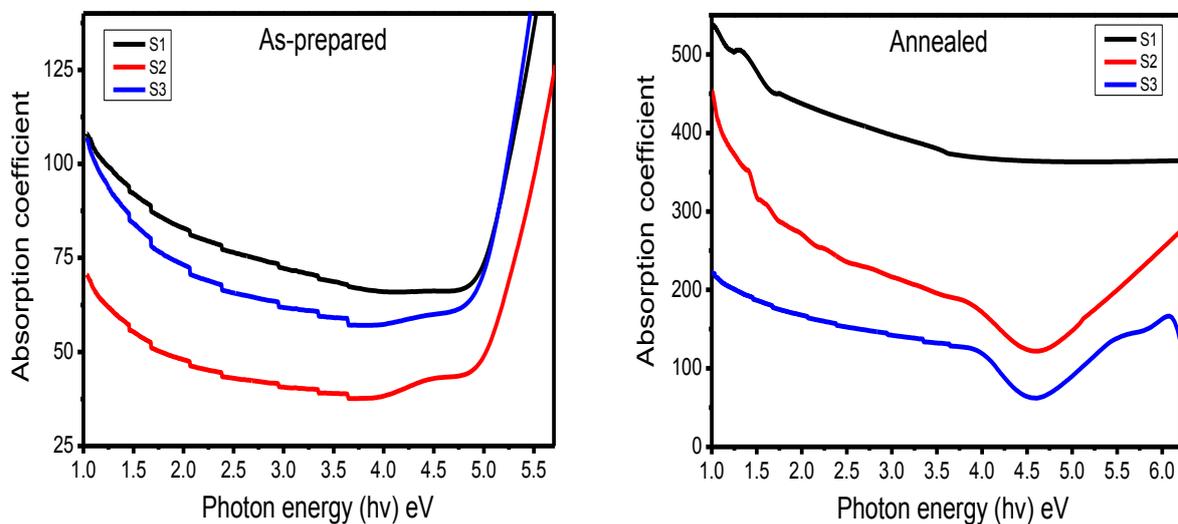


Fig. 3. Absorption coefficient for As-prepared and Annealed samples S1, S2, S3 of $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$

The absorption coefficient of the as-prepared sample S1, S2 and S3 observed in low absorption region and decreases with increasing Cd content in Near ultraviolet region due to defects and impurities. In the same manner absorption coefficient of the thermally annealed sample also decreases with increasing Cd% in NIR region due to structural disorder in localised state of the material. Hence from above conclusion with increasing trends of Cd concentration at decreasing composition of Te with constant Se content, the absorption coefficient of both as-prepared and annealed sample decreases.

2.3.2 Optical Bandgap

The energy at which electron and holes pair is generated is called optical band gap energy. The high absorption region determines the optical band gap energy. The optical energy gap is defined as the intercept of the plot of $(\alpha hv)^{1/2}$ against hv . Fig. 4 shows the optical band gap of as-prepared and annealed sample S1, S2, S3 for $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x = 0, 10, 20$) by direct transition.

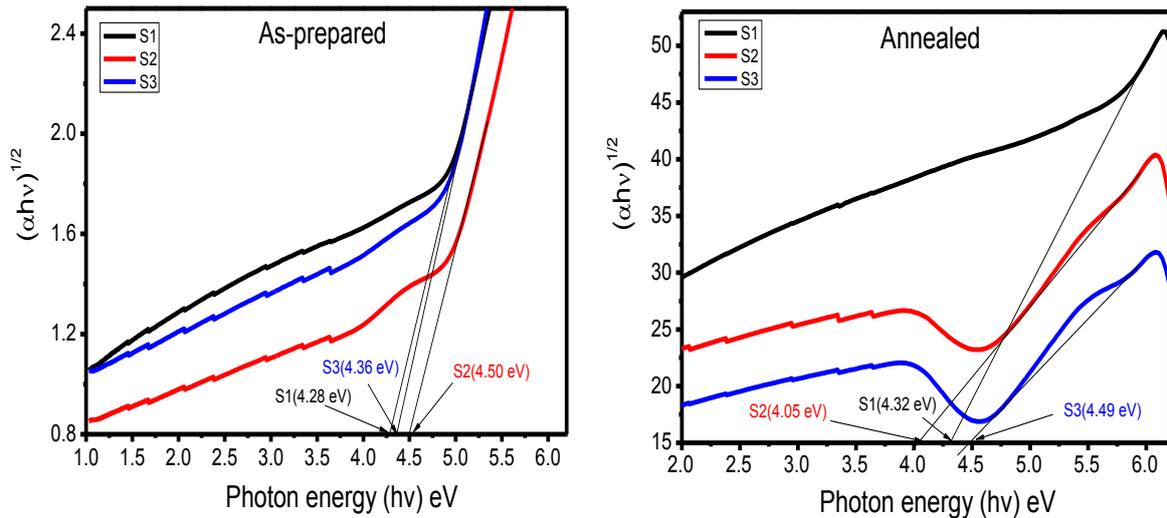


Fig. 4. Optical band gap for As-prepared and Annealed samples S1, S2, S3 of $Te_{90-x}Se_{10}Cd_x$

Expected value of optical band gap for as-prepared and annealed sample S1, S2, S3 are given in Table.1. Optical band gap of the thermally annealed sample has more than that of its as-prepared sample S1, S2 and S3 of $Te_{90-x}Se_{10}Cd_x$ ($x=0, 10, 20$) and increases with increasing concentration of Cd content. Optical band gap of the as-prepared and annealed sample continuously increases as Cd concentration increases in TeSe matrix. The increment in the optical band gap with increasing Cd concentration in the as-prepared and annealed sample of S1, S2, and S3 may be due to the reduction in the disorder and decrease in density of defect states are confirmed by Davis and Mott suggestion (Mott, N. & Davis, E. A., 1970).

2.3.3 Photoluminescence spectroscopy

PL spectra provide the transition energies which can be used to determine electronic energy levels. Fig.5 shows intensity of PL spectra with increasing wavelength of as-prepared and annealed sample S1, S2, S3 of $Te_{90-x}Se_{10}Cd_x$ ($x = 0, 10, 20$) at 330, 380 nm excitation wavelength respectively. In $Te_{90-x}Se_{10}Cd_x$ ($x = 0, 10, 20$), as doping concentration of Cd increases; sample S3 (20% of Cd) of as-prepared sample has maximum intensity than those of S1, S2 observed at 362, 454 and 711 nm. The band at 711 nm might be attributed to the recombination of direct free excitons (Taylor, R. A. & Ryan, J. F. 1987), (Guder, H. S. et al., 2001).

The emission peak intensity of the one in UV region is much more than the one in the red region. In the same manner emission intensity of thermally annealed sample S3 (20%), S2(10%) is more than S1 but much lower than as-prepared sample S1, S2, and S3. Emission spectra of annealed sample S1, S2 and S3 observed at 533 nm in the green region due to oxygen vacancy concentration which increases the defects in the surface of the synthesised materials resulting lowering the PL intensity in the visible region. The major role of electron-photon coupling in the recombination process of a decrease in the intensity at lower energy for thermally annealed samples is due to incomplete absorption whereas a decrease in higher energy for as-prepared sample S1, S2 most likely arises from the energy dependence of the quantum efficiency (Kolobov, A.V. & Tominaga, J., 2012).

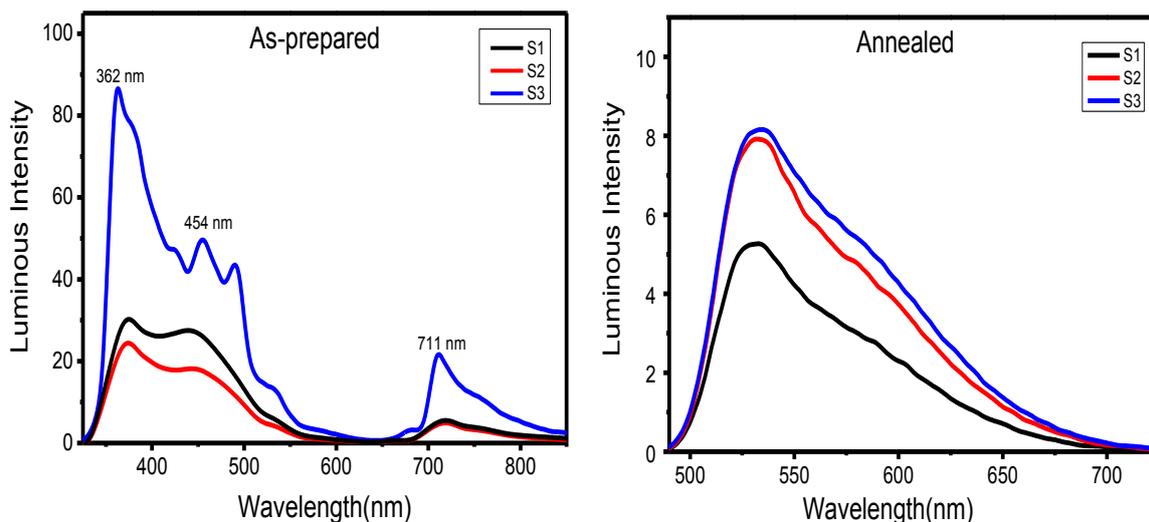


Fig.5. Photoluminescence spectra of As-prepared and Annealed samples S1, S2, S3 for $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$

3. Conclusion

$\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x = 0, 10, 20$) alloys was prepared by melt quenching method. X-ray diffraction results indicated that the entire sample was in the polycrystalline state and a combination of cubic and hexagonal phase and average crystal size of the thermally annealed sample S2 and S3 has much more than that as-prepared sample. FESEM analysis revealed micro-crystallites of the synthesised material. Optical absorption and optical band gap of the as-prepared and thermally annealed sample increases with increasing concentration of Cadmium content. Dislocation density, absorption coefficient and absorption constant of the thermally annealed and as-prepared samples decreases with decreasing Te content as increments of Cd concentration. As the band gap increases the absorption coefficient of the as-prepared and thermally annealed sample decreases. The decrease in energy loss with an increase in Cd concentration of as-prepared and annealed sample S1, S2 and S3 of $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x = 0, 10, 20$) chalcogenide alloys indicates that the charge carriers absorb more energy giving small absorption coefficient which may not be suitable for optical data storage. Optical band gap of as-prepared and annealed sample S1, S2 & S3 of $\text{Te}_{90-x}\text{Se}_{10}\text{Cd}_x$ ($x = 0, 10, 20$) using Tauc's relation possess direct band gap in nature. It is observed that optical energy gap (E_g) increases with increase in the Cd content of chalcogenide alloys which is directly related to the decrease in the density of localised states in the present system. Emission intensity of annealed sample is very small with respect to as-prepared sample which gives the lowest intensity of light in the green region of the visible light due to surface defects in the synthesised materials.

4. Acknowledgement

Financial assistance from UGC New Delhi India vide project F.No 42-773/2013(SR) is gratefully acknowledged. Authors are thankful to U.P State Government for providing XRD facility through Centre of Excellence Scheme at the Department of Physics, University of Lucknow.

References

1. Bruno, B., Pledel, C. B. & Lucas, P. (2009). Forming Glasses from Se and Te. *Molecules*, 14, 4337-4350.
2. Pandey, V. & Tripathi, S. K. (2006). Optical Properties of Amorphous $\text{Se}_{100-x}\text{Sb}_x$ thin films. *J. of Ovonic Research*, 2, 67-76.



3. Fainchtein, R. & Thompson, J. C.(1983).The Optical reflectivity of molten $\text{Se}_x\text{Te}_{1-x}$ alloys. *Physical Review B*, 27.
4. Bureau, B., Danto, S. M., Boussard-Pledel, H. L., Zhang, C. & Lucas, X. H. (2008).Tellurium based glasses a ruthless glass to crystal competition. *Solid State Sci*, 10, 427-433.
5. Sharma, P & Katyal, S. C. (2007).Optical study of $\text{Ge}_{10}\text{Se}_{90-x}\text{Te}_x$ glassy semiconductors. *Thin Solid Films*, 515, 7966-7970.
6. Maan, A. S. & Goyal, D. R. (2008).Dielectric properties of In-Se-Te glassy alloys. *Ind. J. Engg. and Materials Sci*, 15,207-210.
7. Mehra, R. M., Kaur, G., Pundir, A. & Mathur, P. C. (1993). *Jpn. J. Appl. Phys*, 32, 128.
8. Feinleib, J., Deneufville, Moss, J. & Ovshinsky, S. C. (1971). *Appl. Phys. Lett*, 18,254.
9. Yamada, N. O., Nishiuchi, E., Akahira, E., Takao, N. (1991).*J. Appl. Phys*, 69, 2849-2856.
10. Lezal, D., Pedlikova, J. & Zavadila, J. (2004).Chalcogenide Glasses for Optical and Photonics applications. *Optoelectronics and Advanced Materials*, 6, 133-137.
11. Shinde, S. K., Dubal, D. P., Ghodake, G. S., & Fulari, V. J. (2014).Synthesis and characterization of chemically deposited flower-like $\text{CdSe}_{0.6}\text{Te}_{0.4}$ thin films for solar cell application. *Materials Letters*, 126, 17-19.
12. Haoyong, Y., Zhude, X., Jingyi, B., Huahui, B. & Yifan, Z. (2005).Ethylenediamine assisted the growth of single crystal tellurium channels. *Materials Letters*, 59, 3779.
13. Brian. & Younan, X. (2002).One-dimensional nanostructures of trigonal tellurium with various morphologies can be synthesised using a solution-phase approach. *Mater. Chem*, 2, 1875.
14. Bhattacharya, C. & Datta, J. (2007). *J. Solid State Electrochem*, 11,215.
15. Nasir, Md. & Zulfequar, M. (2012).*Open J. of Inorganic Nonmetallic Mat.*, 2, 11-17.
16. Mishra, P. K., Dave, V., Chandra, R., Prasad, J. N. & Choudhary, A. K. (2014). Effect of processing parameter on structural, optical and electrical properties of Photovoltaic chalcogenide nanostructures RF magnetron sputtered thin absorbing films. *Mat.Sci. in Semiconductor Processing*, 25, 307-319.
17. E-Abd El-Wahab. (2000).*Vacuum*, 57, 339.
18. Al-Ghamdi, A. A. (2006).*Vacuum*, 80, 400-405.
19. Halimah, M. K. & Zainal, A. S. (2010).Optical properties of ternary tellurite glasses. *Materials Science-Poland*, 28.
20. Mott, N. & Davis, E. A. (1970).*Electronic processes in non-crystalline materials*. Clarendon Press.
21. Taylor, R. A & Ryan, J. F. (1987). Time-resolved exciton photoluminescence in GaSe and GaTe. *J. Phys. C*, 20, 6175.
22. Guder, H. S., Abay, B., Efeoglu, H., Yogurtu, Y. K. & Lumin, J. (2001).93, 243.
23. Kolobov, A. V. & Tominaga, J. (2012). Properties of Amorphous Chalcogenides.DOI: 10.1007/978-3-642-28705-3_2, Chalcogenides, Springer Series in Materials Science, 164.