

Structural, Morphological and Photoluminescence Studies of As-prepared and Annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ Chalcogenides

Pramesh Chandra¹, Arvind K. Verma², R. K. Shukla³, Anchal Srivastava⁴

^{1,2,3,4}Department of Physics, University of Lucknow, Lucknow – 226007, (U.P.) India

Abstract— The present study is undertaken in order to investigate the influence of addition of copper (Cu) in different proportions on the structural, morphological and photoluminescence properties of as-prepared and annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) chalcogenides. The bulk samples have been synthesized by melt quenching technique from 5N pure constituent elements mixed in proportion of their respective atomic weight percentages. Post-preparation annealing of the three samples has been done at 250 °C.

XRD spectra of the samples show polycrystalline structures with re-arrangement of different crystallites as copper content is varied or annealing is done. Surface morphology remains more or less unchanged. Photoluminescence spectra show that emission is spread in the violet and red regions for as-prepared samples with the undoped sample showing highest PL intensity. Green emission occurs at same wavelength for all the annealed samples. Sample with 10% copper content shows highest PL intensity.

Keywords— Chalcogenide, Copper, Photoluminescence, Surface morphology, XRD.

I. INTRODUCTION

Chalcogenides are a very important class of materials due to their varied technological applications [1-3]. These materials are quite useful for development of active and passive electronic devices. These are low-phonon energy materials and are generally transparent from the visible to infrared region [4, 5].

Chalcogens are elements of group 16 of the periodic table. Among members of this family, selenium (Se) and tellurium (Te) have been studied widely due to their potential applications. These materials have tremendous utility in solar cells, optical limiting, filters, IR emitters, optical rewritable data, IR detectors, antireflection coatings, gratings, optical recording media, etc. Chalcogenide glasses have flexible structure and each atom can adjust its neighbouring environment so that the valance requirements are satisfied. The interest in these materials arises due to their ease of fabrication in the form of both bulk as well as thin films. Se-Te alloys have more advantages than pure chalcogens due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects [6, 7].

Moreover, the physical properties of these alloys depend on their compositions. Addition/doping of a third element like Cu, Bi, Sb, Sn, Pb, Cd, Hg etc. in Se-Te binary alloy is expected to change the properties of the host alloy and behave as a chemical modifier. This produces considerable changes in the characteristics of these materials.

Tellurium-rich alloys have also attracted a lot of attention due to their potential applications. Researchers have reported that tellurium-rich alloys offer good transparency in the infrared region thereby making these glasses a good choice for optical devices. Tellurium-rich glassy alloys of Se-Te are widely used for commercial, scientific, and technological purposes. Their application ranges from optical recording media to xerography [8-10].

The present work intends to study the influence of addition of copper (Cu) in different proportions on the structural, morphological and photoluminescence properties of as-prepared and annealed tellurium-rich chalcogenide $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) bulk samples.

II. EXPERIMENTAL DETAILS

A. Synthesis of bulk samples

Bulk samples $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) are synthesized by melt quenching technique. 5N pure constituent elements – Te, Se and Cu – purchased from Sigma Aldrich are weighed, according to requirement, in proportion of their respective atomic weight percentages using electronic balance having an accuracy of 0.0001 g. The sample-wise respective weighed components are then put in three separate quartz ampoules each having length ~ 8 cm and internal diameter ~ 12 mm. Prior to this, the ampoules are cleaned by rinsing with soap solution, acetone and methanol to avoid the presence of impurities. Vacuum ~ 10^{-3} Torr is maintained by a rotary pump for evacuating the ampoules so as to avoid the reaction of materials with oxygen at high temperatures. During the process of evacuation itself, each ampoule is sealed thermally with the help of oxygen – Liquefied Petroleum Gas (LPG) flame torch.

The sealed ampoules are then placed in a microprocessor-controlled programmable muffle furnace.

Heating is done at the rate of 4°C/min from room temperature upto 1000°C and the ampoules are held at this temperature for 10 hours. During heating, the ampoules are frequently rocked to ensure homogenization and proper mixing of the melt. After 10 hours, the red hot ampoules are taken out from the furnace and quenching of the melts is done by dropping the ampoules immediately into ice-cooled water for the materials to go into glassy state.

The quartz ampoules are then broken and the quenched samples are recovered. The obtained three solid samples are then crushed separately with the help of mortar/pestle and filtered with the help of filter cloth. The process is followed repeatedly till the bulk samples $\text{Te}_{90}\text{Se}_{10}$, $\text{Te}_{80}\text{Se}_{10}\text{Cu}_{10}$ and $\text{Te}_{70}\text{Se}_{10}\text{Cu}_{20}$ are obtained in the form of fine powder.

A part of each final bulk sample is then separated to prepare the annealed samples. Heating is done at the rate of 5°C/min from room temperature upto 250°C and this temperature is maintained for two hours. The samples are then cooled gradually to room temperature. Thus, the three annealed samples are obtained.

B. Characterization of bulk samples

The as-prepared and annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) bulk samples are characterized by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Photoluminescence (PL) spectroscopy. XRD measurements are taken with the help of X-ray diffractometer (Model: Ultima IV from Rigaku, Japan) at a scanning rate of 2°/min employing Cu K_α radiation wavelength 1.54056 Å in the 2θ range 20° – 70°.

Surface morphology is studied by taking images using Field Emission Scanning Electron Microscope (Model: JSM-7610F from JEOL, Japan). Before taking the images, gold-palladium coating is done on the samples with the help of auto fine coater (Model: JEC-3000FC from JEOL, Japan). Photoluminescence (PL) spectra are recorded with the help of Fluorescence spectrometer (Model: LS55 Perkin Elmer). All the measurements are performed at room temperature.

III. RESULTS AND DISCUSSION

A. X-ray Diffraction (XRD)

Figure 1 (a), (b), (c) show XRD patterns of the as-prepared $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ bulk samples for $x = 0, 10, 20$ respectively. All the samples show polycrystalline structure.

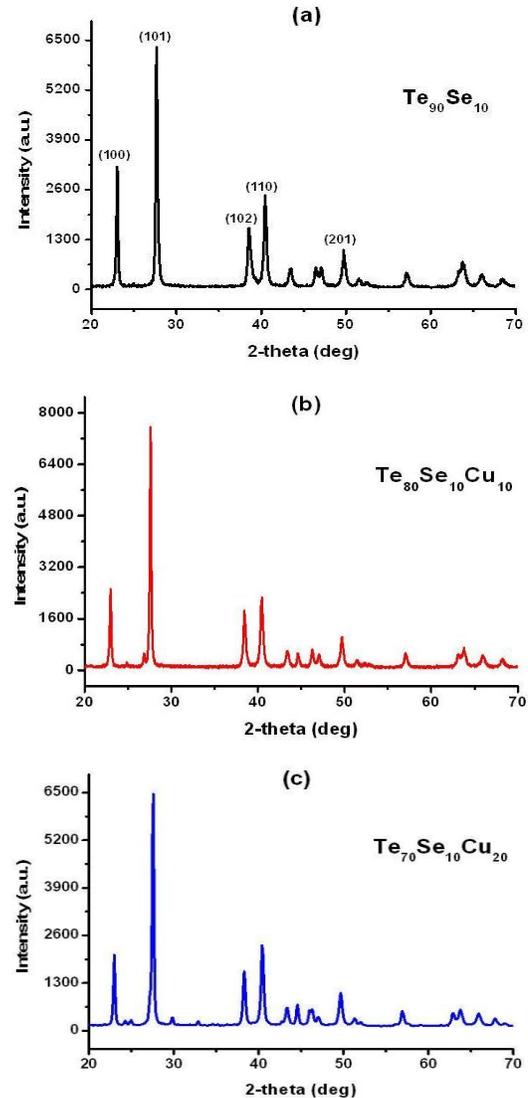


Figure 1. XRD spectra of as-prepared $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ bulk samples for (a) $x = 0$, (b) $x = 10$ and (c) $x = 20$

For $x = 0$, the prominent peaks are at angular positions 23.05°, 27.60°, 38.56°, 40.44° and 49.75° which correspond to (100), (101), (102), (110) and (201) planes respectively of tellurium [11]. Most intense peak is found to be along (101) plane. Some minor peaks are also seen.

With 10% copper content, i.e. $x = 10$ in the form of $\text{Te}_{80}\text{Se}_{10}\text{Cu}_{10}$ sample, the XRD pattern shows prominent peaks at angular positions 23.02°, 27.57°, 38.47°, 40.41° and 49.73°.

These positions are at nominally lower angular positions as compared to the $x = 0$ case. The planes corresponding to these positions are the same as earlier i.e. (100), (101), (102), (110) and (201) respectively of tellurium. The intensity of peak along plane (101) is maximum and also more as compared to the $\text{Te}_{90}\text{Se}_{10}$ case.

For $x = 20$, major peaks are found at angular positions 22.95° , 27.54° , 38.31° , 40.36° and 49.69° which show further shift towards lower side as compared to $x = 10$ case. The planes are the same as discussed earlier. The most intense peak is still along (101) plane. Redistribution of peak intensities implies re-arrangement of crystallites along different planes. Peaks corresponding to the added metal do not appear at all.

Figure 2 (a), (b), (c) show XRD patterns of the annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ bulk samples for $x = 0, 10, 20$ respectively. All the samples again show polycrystalline structure. For $x = 0$, the prominent peaks are found at angular positions 23.10° , 27.68° , 38.61° , 40.46° and 49.77° . This shows that annealing shifts the positions of peaks towards slightly higher values as compared to the as-prepared case. From [11], it can be said that the planes corresponding to these positions are (100), (101), (102), (110) and (201) respectively of tellurium. Most intense peak is maintained along (101) plane. There is not much difference in intensities of the peaks between the as-prepared and annealed samples.

For $x = 10$ i.e. with introduction of 10% copper, XRD spectra of the annealed $\text{Te}_{80}\text{Se}_{10}\text{Cu}_{10}$ bulk sample shows prominent peaks at angular positions 23.10° , 27.71° , 38.51° , 40.51° and 49.75° . Annealing again shifts angular positions to higher values. The planes also remain the same with intensity along (101) plane still found to be maximum. The intensities along different planes show an increase as compared to those of the as-prepared sample.

For $x = 20$, the peaks are found at angular positions 23.07° , 27.61° , 38.35° , 40.48° and 49.71° . These positions are again at higher values as compared to those of the as-prepared sample. The planes are the same as before i.e. (100), (101), (102), (110) and (201) respectively of tellurium. In this case, too, the intensities along different planes show an increase as compared to those of the as-prepared sample. Re-arrangement of crystallites occurs due to annealing which results in modification in crystallization [12]. Peaks of the doped metal Cu do not appear in the XRD spectra of annealed samples, too.

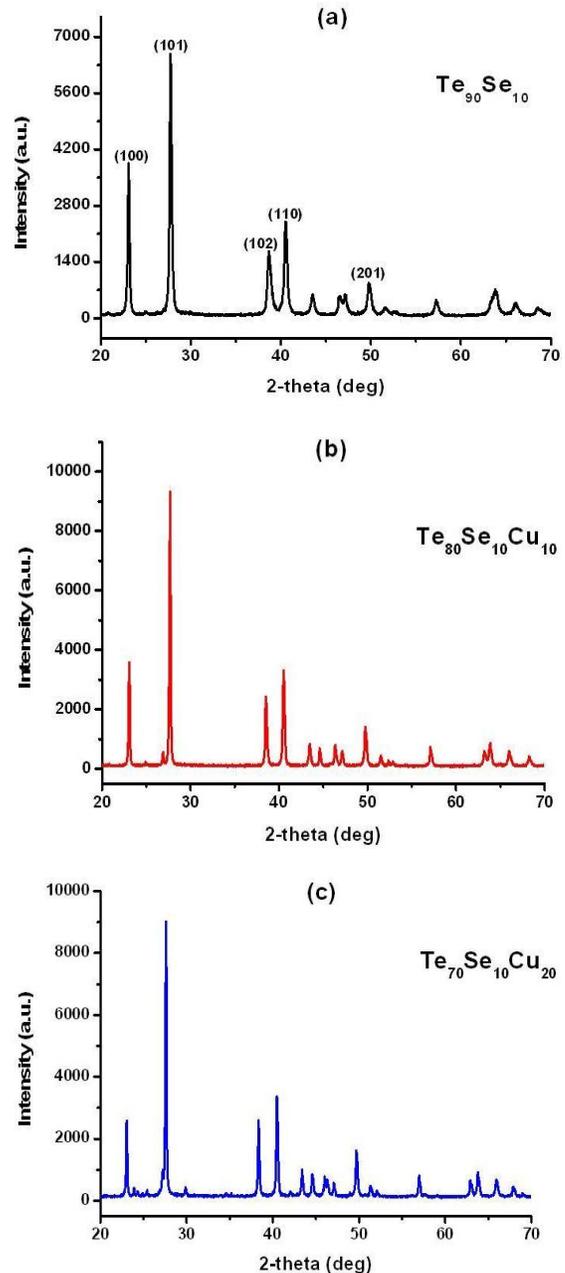


Figure 2. XRD spectra of annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ bulk samples for (a) $x = 0$, (b) $x = 10$ and (c) $x = 20$

Table I shows angular positions of peaks of the as-deposited and annealed bulk samples with varying contents of copper. This gives a clear picture of the shifting of angular positions in the various samples with increasing copper content and also due to annealing.

TABLE I
ANGULAR POSITIONS OF XRD PEAKS FOR AS-PREPARED AND ANNEALED $Te_{90-x}Se_{10}Cu_x$ SAMPLES

	x = 0	x = 10	x = 20
AS- PREPARED	23.05°	23.02°	22.95°
	27.60°	27.57°	27.54°
	38.56°	38.47°	38.31°
	40.44°	40.41°	40.36°
	49.75°	49.73°	49.69°
ANNEALED	23.10°	23.02°	23.07°
	27.68°	27.71°	27.61°
	38.61°	38.51°	38.35°
	40.46°	40.51°	40.48°
	49.73°	49.75°	49.68°

The crystallite size along the planes, as shown in table II, is determined by the Debye-Scherrer formula [13],

$$d = K \lambda / \beta \cdot \cos \theta$$

where d is the average crystallite size, $K = 0.9$, $\lambda_{Cu-K\alpha} = 1.54056 \text{ \AA}$, β – Full Width at Half Maximum in radians, θ – Bragg angle.

Table II
Crystallite Size Along Different Planes

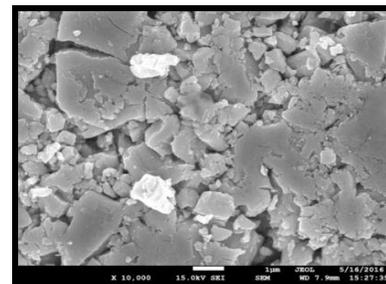
		x = 0	x = 10	x = 20
(100)	(a)	43.2	43.3	42.6
	(b)	37.8	58.1	59.8
(101)	(a)	39.2	49.0	45.9
	(b)	35.1	58.6	68.1
(102)	(a)	24.6	32.5	28.9
	(b)	19.2	46.8	59.6
(110)	(a)	24.2	25.1	30.6
	(b)	27.8	42.8	55.3
(201)	(a)	20.0	25.1	23.8
	(b)	20.9	39.2	48.6

(a) as-prepared sample
(b) annealed sample

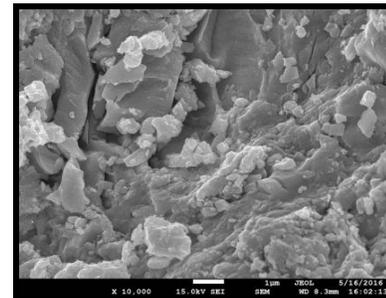
It is clear from table II that the crystallite size varies in accordance with variations in peak positions due to annealing along different prominent planes for a particular value of x.

B. Surface morphology

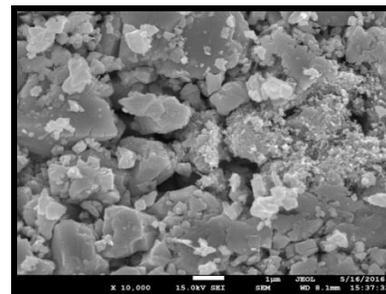
In Field Emission Scanning Electron Microscopy (FESEM), the electrons interact with atoms in the sample, which produce various signals that can be detected. This gives important information regarding growth mechanism, shape and size of the grains. Figure 3 (a), (b), (c) show FESEM images of the as-prepared bulk samples $Te_{90-x}Se_{10}Cu_x$ for x = 0, 10 and 20 respectively. Similarly, Figure 4 (a), (b), (c) show FESEM images of the annealed samples for x = 0, 10 and 20 respectively.



(a)



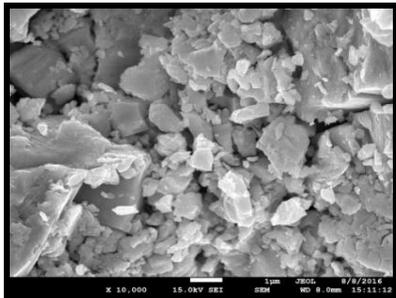
(b)



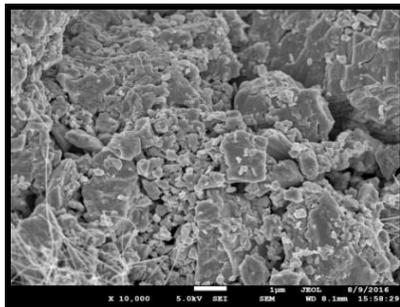
(c)

Figure 3. FESEM images of as-prepared $Te_{90-x}Se_{10}Cu_x$ bulk samples for (a) x = 0, (b) x = 10 and (c) x = 20

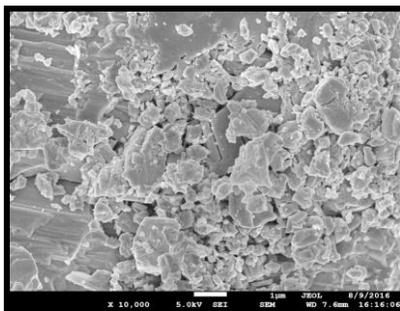
It is observed that there is not much change in the surface morphology of the as-prepared as well as annealed samples with changing copper content. It is evident that images of the as-prepared and annealed samples are uniform and without any pinholes or cracks, which shows the presence of some nano and micro-crystallites of the synthesised material.



(a)



(b)



(c)

Figure 4. FESEM images of annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ bulk samples for (a) $x = 0$, (b) $x = 10$ and (c) $x = 20$

A. Photoluminescence (PL) Spectra

Photoluminescence spectroscopy gives information with respect to the different energy states that are available between valence and conduction bands and are responsible for radiative recombination [14]. PL spectra have been recorded at 330 nm excitation wavelength (λ_{ex}).

Figure 5 shows PL spectra of the as-prepared bulk samples $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$). All the samples show two emission bands.

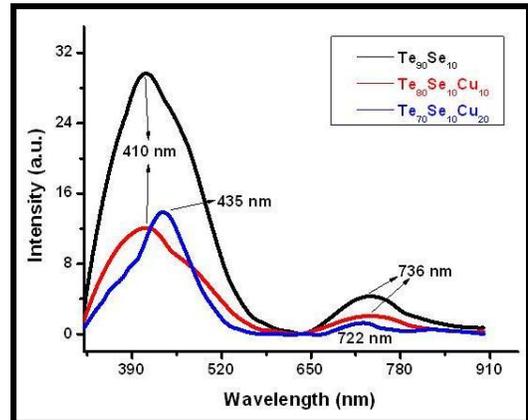


Figure 5. PL spectra of as-prepared $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) bulk samples

For $x = 0$, emission is found to occur at 410 nm and 736 nm which fall in the violet and red regions respectively of the visible spectrum. Similarly, for $x = 10$, emission is again found to occur at 410 nm and 736 nm, but with reduced PL intensities.

With 20% copper content, emission bands occur at 435 nm and 722 nm. Thus, it is clear that emission is spread in the violet and red regions with varying copper content. PL intensities are much higher in the violet region as compared to the ones in the red region. Clearly, PL intensities are highest for $\text{Te}_{90}\text{Se}_{10}$ ($x = 0$) case.

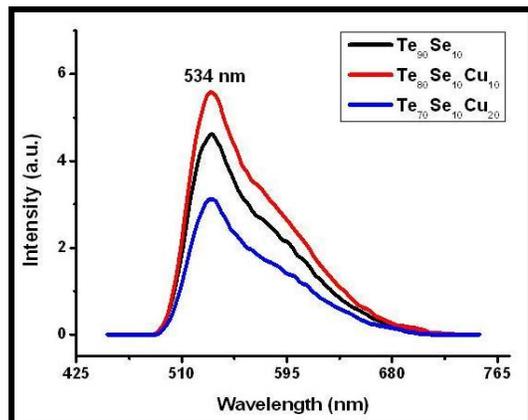


Figure 6. PL spectra of annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) bulk samples

Figure 6 shows PL spectra of annealed $\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ bulk samples. It at once becomes clear that emission occurs at 534 nm for all the values of x . PL emission now falls in the green region. PL intensities are found to be highest for the sample with 10% copper content while it is lowest for the sample with 20% content.

Annealing modifies the local electron distribution which changes the number of surface states involved in PL emission. This is quite likely to occur in view of modifications observed in crystalline structures.

IV. CONCLUSIONS

$\text{Te}_{90-x}\text{Se}_{10}\text{Cu}_x$ ($x = 0, 10, 20$) bulk samples were synthesized using melt quenching method from 5N pure elements as constituents mixed in proportion of their respective atomic weight percentages. Post-preparation heat treatment was given at 250°C for two hours. The XRD patterns of both the as-prepared and annealed samples indicate polycrystalline structures. There is re-arrangement of crystallites along different planes with changing copper content and also due to annealing.

The FESEM images show that there is not much change in the surface morphology and somewhat uniform nature of the grains is found. At 330 nm excitation wavelength, PL emission is observed to be spread in the violet as well as red regions for the as-prepared samples with varying PL intensities. Green emission is observed at same wavelength for the annealed samples with the sample having 10% copper content showing highest PL intensity. The samples are useful for applications in electronics and optoelectronics.

Acknowledgements

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

REFERENCES

- [1] Zakery A. and Elliott S. R., Journal of Non-Crystalline Solids, 330 (2003) 1 – 12.
- [2] Kumar A., Lal M., Sharma K., Tripathi S. K. and Goyal N., Indian Journal of Pure and Applied Physics, 51 (2013) 251 – 253.
- [3] Kumar A., Lal M., Sharma K., Tripathi S. K. and Goyal N., Chalcogenide Letters, 9 (2012) 275 – 285.
- [4] Savage J. A., Infrared Optical Materials and their Antireflection Coatings, Adam Hilger Ltd.: Bristol, (1985).
- [5] Sharma K., Lal M., Kumar A. and Goyal N., Journal of Ovonic Research, 10 (2014) 7 – 13.
- [6] Shimakawa K., Philosophical Magazine B, 46 (1982) 123 – 135.
- [7] Kasap S. O., Wagner T., Aiyah V., Krylouk O., Bekirov A. and Tichy L., Journal of Materials Science, 34 (1999) 3779 – 3787.
- [8] Desevedavy F. et al., Applied Optics, 48 (2009) 3860 – 3865.
- [9] Michel K. et al., Journal of Non-Crystalline Solids, 326 (2003) 434 – 438.
- [10] Ohta T., Journal of Optoelectronics and Advanced Materials, 3 (2001) 609 – 626.
- [11] Powder Diffraction Data File, Joint Committee of Powder Diffraction Standard, International Center for Diffraction Data, USA card no. 00-004-0554.
- [12] Kale R. B. and Lokhande C. D., Semiconductor Science and Technology, 20 (2004) 1–9.
- [13] Cullity B. D. and Stock S.R., Element of X-ray diffraction. Adison – Wesley Publishing Company, 1 (1956) 531.
- [14] Nogriva V., Dongre J. K., Ramrakhiani M. and Chandra B. P., Chalcogenide Letters, 5 (2008) 365 – 373.