A study of some physico-chemical properties in amorphous Se-Ag alloy prior to and subsequent to Laser-stimulated nano-structuring

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Nano-materials and Nano-technologies have attracted tremendous attention of researchers in recent time. New physical properties and new technologies both in sample preparation and device fabrication evoke on account of the development of nano-science. The present work is our novel attempt in this direction. Formation of silver nano-rods by laser interaction in glassy Se$_{98}$Ag$_2$ alloy has been successfully achieved. Laser irradiated changes in electrical and optical property of glassy Se$_{98}$Ag$_2$ alloy have also been studied. We have determined dc conductivity, optical band gap and micro-hardness of unexposed and exposed samples of binary Se$_{98}$Ag$_2$ alloy. Thermal behaviour of unexposed and exposed samples is observed using differential scanning calorimetry (DSC). Phases of laser exposed binary Se$_{98}$Ag$_2$ alloy have been confirmed by XRD technique. Optical UV/VIS absorption spectra as a function of photon energy in the wave length region 200–1100 nm is studied. Raman spectrum and FT-IR spectrum of the samples have been examined before and after laser irradiation.

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1. Introduction

New classes of nano-materials have created a technological revolution in the present era. The common ground for these materials, and the devices made from them, is that they are constituted of building blocks of metals, ceramics or polymers that are nanometer size (1-100 nm) objects. The properties of such materials are novel and can be tailored by controlling the dimensions of their building blocks and assembly via physical, chemical or biological methods. Laser-assisted nano-structuring of exotic materials has gained a lot of interest in the research field recently [1-6].

Chalcogenide semiconducting glasses are principally well-known and promising materials, due to their low phonon energy, extended infrared transparency, high refractive index, high photosensitivity and reversible phase change optical recording etc [7]. These glasses are potential candidates as core materials for light transmission in optical fibers, when short wave lengths and flexibility are required. Chalcogenides (ChGs) exhibit a unique property of reversible transformation. This property makes them very useful in optical memory devices. Amorphous-crystalline phase transition utilizes the large optical reflectivity which is used in the optical storage [8-11].

The synthesis of new materials made of particles, rods and wires with dimensions in the nano-meter scale is among the most active areas of research in science due to the unique properties of these materials compared to conventional materials made from micron sized particles. In recent year, nano-structuring of metal chalcogenides have gained increasing interest due to their promising applications in different areas [12-19]. Metal chalcogenides in the form of Nano-clusters, nano-wires, nano-sheets and nano-plates have been developed to explore their new functionalities and emergent properties [12-19]. In silver chalcogenides, especially silver selenide (Ag$_2$Se) has been found very useful intriguing properties [15-19]. It is a mixed conductor with high electronic and ionic mobility, high electrical conductivity, large Seebeck coefficient, and low thermal conductivity. These features make Ag$_2$Se useful as a photo-sensitizer in photographic films and thermochromic materials [20].

The changes obtained in optical absorption in some semiconducting glassy systems are due to heat treatment or laser irradiation. An additional striking and unique property of semiconducting ChG glasses is their ability to undergo structural changes upon irradiation with an appropriate laser source [8-11]. Laser exposed glassy materials are widely used to improve physic-chemical properties. Basically, a lateral growth is stimulated by intensity profiles, which leads to crystallization along the temperature gradient of the melt. Laser crystallization increases the carrier mobility in chalcogenide materials. Thus, it is a issue of systematic and logical investigations for the better understanding of the mechanism related with the phenomena taking place in them as well as their practical applications [21-23]. To attain low operating power for all-optical processing of high data rate telecommunication signals, one has to develop a progression to increase the nonlinear optical interaction of chalcogens with other elements and compounds [24].
Silver selenide has received considerable attention owing to their attractive physico-chemical properties. Though, the properties of bulk Ag2Se have been studied comprehensively in the bulk, yet very few reports are available on Ag2Se at nano-scale. Literature survey clearly shows that the investigations on nano-structuring of silver chalcogenide are insufficient as compared to cadmium and zinc chalcogenides. In past, some attempts have been made to obtain Ag2Se in the form of nano-particles [25, 26] nano-wires [27] and nano-scale dendrites [28].

In the light of above facts, we have started novel work in this direction. Recently, a single-step synthesis of Ag2Se crystals in the form of nano-rods using laser-induced crystallization of glassy Se98Ag2 alloy as base material is reported by us [29]. This route is beneficial over the other non-conventional routes for the reason that it utilizes normal temperature, atmospheric pressure and standard chemicals. It is complete within a few minutes.

In semiconducting chalcogenide glasses, the crystal sizes are no longer dominated by randomly distributed nucleation centres. The ability to selectively melt an amorphous layer through the absorption of a short laser pulse has made pulsed laser crystallization of amorphous films, a standard technique for the fabrication of large area polycrystalline films on low cost substrates. Laser exposure has also been applied to re-crystallize an amorphous thin film on a crystalline substrate [30, 31]. Our present work is the extension of our previously published work [29]. It has been found that laser irradiation changes the physical properties of the material which are strongly dependent on the internal structure of absorbed substance. Therefore, we have focused our attention on some physical properties of the proposed base material.

2. Experimental procedure

Binary glassy Se98Ag2 alloy was prepared by quenching technique using 5N pure Se and Ag elements under suitable experimental conditions. After proper weighing of Se and Ag elements using an electronic balance (least count 10^-5), the materials were sealed in evacuated (~ 10^-6 Torr) quartz ampoules (length ~ 5 cm and internal diameter ~ 8 mm). The vacuum (~ 10^-6 Torr) was achieved using high Vacuum pumping system (Hindhivac, Model: VS65D). The ampoule was kept inside the furnace at 1000 °C (where the temperature was raised at a rate of 3-4 °C/min.). During heating, the ampoule was constantly rocked by rotating a ceramic rod with which the ampoule was tucked. This was done to obtain homogeneous glassy alloy. After rocking for about 12 hours, the obtained melt was cooled rapidly by removing the ampoule from the furnace and dropping to ice-cooled water rapidly. The ingot of the sample was then taken out by breaking the quartz ampoules.

The glass, thus prepared, was irradiated (~ 30 seconds) by cw Nd: YVO4 laser [Model: Verdi-V5 (USA)] operating at wavelength 532 nm and maximum pulse energy 5.5 W. The unexposed and exposed samples of Se98Ag2 glass were ground to make fine powder for DSC studies. 10 to 20 mg of the powder was heated at constant heating rate and the changes in heat flow with respect to an empty reference pan were measured. The thermal behaviour of unexposed and exposed samples was investigated using differential scanning calorimeter (Sindazu, Japan). The temperature precision of this equipment is ± 0.1 K with an average standard error of about ± 1 K in the measured values (glass transition and crystallization temperatures).

DSC scans of unexposed and exposed samples of binary Se98Ag2 alloy at heating rate of 15 K/min are shown in Fig. 1. From this figure, it is clear that unexposed sample shows the well-defined endothermic peaks at the glass transition temperature (Tg) and melting temperature (Tm). An exothermic peak at crystallization temperature (Tc) is also located between glass transition and melting peaks. However, only one endothermic peak corresponding to melting temperature (Tm) is observed for the exposed sample. The respective endothermic and exothermic peaks corresponding to glass transition temperature (Tg) and crystallization temperature (Tc) are disappeared for exposed samples (see Fig. 1). This is the clear indication of laser-induced crystallization of exposed sample.

![DSC scans of unexposed and exposed samples of binary Se98Ag2 alloy at heating rate of 15 K/min.](image)

**Fig. 1**

For optical measurement, the absorption spectra of unexposed and exposed samples were obtained by using UV-Vis-NIR 3200 spectrometer. A Micro Raman set-up consists of a 514.5 nm Ar+ laser delivering about 5 mW intensity as an excitation source and spectrometer (Renishaw RM 1000) having spectral resolution of ~1 cm^-1 were used for the analysis of Raman bands and intensity. The transmission spectra of unexposed and exposed samples were investigated using FT-IR spectroscopy (PerkinElmer spectrum 65, FT-IR spectrometer; PerkinElmer, MA). Micro-indentation measurement was performed on the unexposed and exposed specimens using an automated digital Vickers micro-hardness tester (Vaiseshika Electron Devices, India; Model: DHV-1000).
3. Results and discussion

It is well known that the laser irradiation produces defects in the chalcogenide glasses. Wagner et al. [32] have shown the optically induced crystallization in amorphous Ag$_x$(Sb$_{0.33}$S$_{0.67}$)$_{100-x}$ films, and studied the Ar laser effect of silver content in the host materials with modified optical and structure properties of the thin films. Toet et al. [33] have obtained the pulse laser crystallization and structuring of a-Ge on GaAs. Al-Ghamdi et al [34] have performed the study of laser-induced changes on optical band gap of amorphous and crystallized thin films of Se$_{75}$S$_{25-x}$Ag$_x$ alloys. The investigation on femto-second laser-induced micro features in glasses is reported by Qiu et al. [35]. Writing of crystal line patterns in glass by laser irradiation is successfully demonstrated by Honma et al [36].

Laser exposure may cause excitation of the electron of atoms, and possibly, displacement of atom from their lattice sites. These new electronic arrangements cause a change in the optical and electrical properties [37-39]. In amorphous materials like ChG glasses, the relation between electronic properties and disorder is very interesting [40-43]. Parthasarathy et al [44] have reported the electrical conductivity of bulk Se$_{1-x}$Te$_x$ glasses as a function of pressure (up to 8 GPa) and temperature (down to 77 K). DC conductivity of chalcogenide glasses using extended pair model is obtained by Prakash et al [45]. The effect of structure on the dc electrical conductivity of selenium from 300 to 600 K through thermal analysis at the field strengths below 100 Vcm$^{-1}$ is performed by Murphy et al [46].

From above discussion, it is clear that the presence of defects and irradiation-induced disorder in amorphous materials affect the characteristic features of their physico-chemical properties in a significant way. Here we have investigated some physico-chemical properties of unexposed and exposed samples of Se$_{98}$Ag$_2$ glass.

3.1 Structural analysis

The structure of the unexposed and exposed samples was verified by X-ray diffractometer using CuK$_\alpha$ radiation ($\lambda = 1.5405$ Å). The X-ray tube voltage and current were 30 kV and 20 mA respectively. The scan range was 5° – 80° (2$\theta$) and the scan speed was 1°/min [29]. From Fig. 2, one can see that the XRD pattern of unexposed sample reveals no sharp diffraction lines. This indicates that the unexposed Se$_{98}$Ag$_2$ alloy is in glassy or amorphous phase. However, the XRD pattern of exposed sample indicates that three crystalline phases belong to Se (hexagonal), Ag (cubic, FCC) and Ag$_2$Se (cubic, FCC) are grown. Fig. 2 clearly shows that the new phases are generated in the amorphous matrix of Se$_{98}$Ag$_2$ alloy after laser exposure. Surface morphology of both unexposed and exposed samples was characterized by Scanning Electron Microscope SEM photographs of unexposed and exposed samples are shown in Fig. 3(a) and 3(b) respectively [29]. From these photographs, an enormous laser-induced structural transformation in binary Se$_{98}$Ag$_2$ alloy is observed. Agglomerated structure shown in Fig. 3(a) indicates the amorphous structure of Se$_{98}$Ag$_2$ alloy. But the formation of new phases in the form of nano-rods through nucleation and growth can be seen in Fig. 3(b). From this figure, it is also clear that the surface morphology is still amorphous but there is a localized formation of nanocrystallites due to laser exposure in the form of rods of different lengths and diameters. Elemental confirmation of both samples is done by energy dispersion spectrometer (EDX) as shown in Fig. 4. From this figure, one can see that the respective atomic composition of selenium and silver is found nearly 98.14% and 1.86%.
3.2 dc conductivity analysis

In chalcogenide semiconductors, the conduction mechanism is governed by three processes: namely, transfer of charge carrier between delocalized state in the conduction band (E > E_c) and valence band (E < E_v), transitions of charge carriers in the band tails and hopping of charge carriers between delocalized states in the bands near the Fermi level (E_f) [47, 48]. The conduction in chalcogenide glasses is intrinsic [49] and that the Fermi level is close to the midway of the energy gap. This intrinsic conduction is determined by carrier hopping from the states close to the edge of the valence band to localized states near the Fermi level or from the state near the Fermi level to the conduction band. Depending on the dominant process, one may decide the suitable conduction mechanism. The Fermi level is somewhat shifted from the middle of the energy gap towards the valence band in case of amorphous systems [50].

In the present work, we have studied temperature dependence of dc conductivity for unexposed and exposed samples of binary Se_98Ag_2 alloy. Fig. 5 and 6 show the current-voltage (I-V) characteristics of unexposed and exposed samples. The dc conductivity at different temperatures is evaluated using I-V plots of both samples. The plots of ln σ versus 1000 / T for unexposed and exposed samples are shown in Fig. 7. From this figure, we observe that both plots are the straight line. This indicates that the conduction in unexposed and exposed samples is through a thermally activated process. The dc conductivity of both samples is therefore expressed by the usual relation:

\[ \sigma = \sigma_0 \exp \left( -\frac{\Delta E}{k_B T} \right) \]

Where \( \Delta E \) is the activation energy, \( \sigma_0 \) is the pre-exponential factor and \( k_B \) is Boltzman constant. The values of activation energy \( \Delta E \) and pre-exponential factor are calculated using slopes and intercepts of these straight lines shown in Fig. 7. The estimated values for unexposed and exposed samples are given in Table 1. From Table 1, it is clear that values of both \( \Delta E \) and \( \sigma_0 \) are almost same for unexposed and exposed samples and there is no significant change in the values \( \Delta E \) and \( \sigma_0 \). This is obvious due to the fact that laser was exposed on the microscopic area of the specimen. The estimated values of pre-exponential factor are \( 0.16 \times 10^2 \, \Omega^{-1} \text{cm}^{-1} \) and \( 0.15 \times 10^2 \, \Omega^{-1} \text{cm}^{-1} \) for unexposed and exposed samples. The magnitude of \( \Delta E \) and \( \sigma_0 \) in the present work indicate that the conduction is due to thermally assisted tunnelling of charge carriers in the localized states present in the band tails. Here, the activation energy alone does not provide any information as to whether conduction takes place in the extended states above the mobility edge or by hopping in the localized states. This is due to the fact that both of these conduction mechanisms may take place simultaneously. These two conduction mechanisms can be distinguished on the basis of the value of pre-exponential factor \( \sigma_0 \). It was suggested by Mott [51] that the pre-exponential factor, \( \sigma_0 \), for conduction in the localized states should be two to three orders smaller in magnitude than that of the conduction in the extended states. It becomes even smaller for conduction in the localized states near the Fermi level. For the conduction in extended states, the value of pre-exponential factor, \( \sigma_0 \), reported for a-Se and other Se based alloy is of the order of \( 10^4 \, \Omega^{-1} \text{cm}^{-1} \) [52]. Pre-exponential factor, \( \sigma_0 \), in glassy Se-Ag system has the order of \( 10^2 \, \Omega^{-1} \text{cm}^{-1} \). Therefore, the possibility of extended state conduction is completely ruled out and localized states conduction in the tail states is likely to take place [53]. Khan et al [54] have also suggested the localized states conduction in their system on the basis of low value of pre-exponential factor, \( \sigma_0 \).
3.3 Optical analysis

The study of UV/VIS optical absorption spectra in glassy and laser induced Se$_{98}$Ag$_2$ alloy provides essential information about the band structure and energy gap. The lower energy part of the spectrum gives information about the atomic vibrations, whereas the higher energy part of the spectrum gives information about the electronic state. In fact, there are three kinds of absorption mechanism in solids: (i) free carrier absorption, (ii) lattice absorption and (iii) electronic inter-band absorption.

In the phenomenon of absorption, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge. Fig.8 shows absorption spectra of glasses where the electronic absorption edge was located at 320 nm and 250 nm, for glassy and laser exposed Se$_{98}$Ag$_2$ alloy, respectively. It is observed that, $\alpha$ decrease with increasing wavelength or decreasing energy. It is seen that the position of fundamental absorption edge shifts to higher wavelength after laser irradiation. The exponential law of absorption of light, $I = I_0 \exp(-\alpha d)$ [55] is used to characterise absorption coefficient, $\alpha$.

$$\alpha = 2.303 \left( \frac{A}{d} \right)$$

Where $A = \log (I/I_0)$ since $I_0$ and $I$ are the intensity of the incident and transmitted light, respectively and, $d$ is the thickness of glassy sample. In high absorption region, the absorption coefficient of Se$_{98}$Ag$_2$ alloy follows the relation:

$$(\alpha h\nu) = B (h\nu - E_{g}^{opt})^n$$

Here, $B$ is the band edge parameter that depends on transition probability, $E_{g}^{opt}$ is the optical band gap, $n$ is the exponent and has the value 2, which defines the indirect transtion process. The usual method for calculating band gap, $E_{g}^{opt}$ involves plotting of $(\alpha h\nu)^{1/2}$ versus $h\nu$, a spectral variation in $(\alpha h\nu)^{1/2}$ over $h\nu$, as shown in Fig.9. The observed value of $E_{g}^{opt}$ for glassy and laser exposed and unexposed samples can be described by eq. (3) is specified in Table 1. In Fig.9, we see that the band gap is going to shift at lower value, after the laser irradiation on glassy Se$_{98}$Ag$_2$ alloy. The change in optical energy gap from glassy to laser exposed system could be determined by identification of the transformed phase.
Table 1. Some physical properties of unexposed and exposed Se98Ag2 alloy

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Unexposed Se98Ag2</th>
<th>Exposed Se98Ag2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity $\sigma$ $(\Omega\cdot\text{cm})^{-1}$</td>
<td>6.1 E-11</td>
<td>1.6 E-10</td>
</tr>
<tr>
<td>Activation energy of dc conduction $\Delta E$ (eV)</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>Optical band gap $E_{g}^{\text{opt}}$ (eV)</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Micro-hardness $H_V$ (kgf/mm²)</td>
<td>63.4</td>
<td>67.9</td>
</tr>
<tr>
<td>Module of elasticity $E$ (kgf/mm²)</td>
<td>950.4</td>
<td>1018.9</td>
</tr>
</tbody>
</table>

These results are interpreted in terms of localized states due to shift in Fermi level. The optical absorption also depends on short-range order in the glassy states and defects associated with it, the decrease in optical band gap may be explained on the basis of “density of state model” proposed by Mott and Devis [56]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the glassy structure. Unsaturated bonds present in the system are responsible for the formation of some of the defects, producing localized states in the amorphous solids. The presence of high concentration of localized states in the band structure is probably responsible for the low values of optical band gap in the laser exposed Se98Ag2 alloy.

Evolution of Raman spectra as a function of energy in term of wave number (200-1000 cm⁻¹) with decreasing intensity of illumination after laser irradiation is shown in Fig. 10. The spectra of the glassy Se98Ag2 alloy is close to that of glassy Se, the only additional feature observed is the appearance of the 455 cm⁻¹ band of Se-Ag (Ag₂Se). But the spectrum of laser irradiated sample is different only by intensity with pure glassy Se98Ag2 alloy. Observed frequency 233 cm⁻¹ in Fig. 10 has the symmetry of E mode in fundamental Raman peak [57]. Raman bands 233 cm⁻¹ (strong) and 437 cm⁻¹ (broad and weak) are assigned for Se-Se bonds and 455 cm⁻¹ for Se-Ag (Ag₂Se), respectively [58].

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Fig. 10

Fig 11 (a) and (b) show the FT-IR transmittance results of glassy and laser irradiated Se98Ag2 alloy. Absorption peaks of Se-Se and Se-Ag are observed in the wave number region 500-4000 cm⁻¹ for Se98Ag2 alloy. Some frequency bands 582.1 cm⁻¹, 1024.9 cm⁻¹, 1383 cm⁻¹, 1432.9 cm⁻¹, 2919.1 cm⁻¹, 3444.2 cm⁻¹ are shifted from the position after the laser irradiation of glassy Se98Ag2 system. The band at 1630.2 and 1740.9 cm⁻¹ are very intense in laser irradiated Se98Ag2 system but stretching mode at 1636 and 1727 cm⁻¹ are not much intense in glassy Se98Ag2. The band present at 1630.2 cm⁻¹ and 1636 cm⁻¹ assigns H₂O bending mode. Vibration frequency, 3435.9 cm⁻¹ and 3444.2 cm⁻¹ reveals the presence of H-O-H stretching mode for laser irradiated and glassy sample, respectively, it may be during the sample preparation for FT-IR. All observed Modes of vibration of selenium and selenium-silver system, before and after laser irradiation are listed in Table 2.
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Table 2. Mode of vibration before and after laser irradiation in Se$_{98}$Ag$_{2}$ alloy

<table>
<thead>
<tr>
<th>Mode of vibration of glassy Se (cm$^{-1}$)</th>
<th>Mode of vibration before laser irradiation in Se$<em>{98}$Ag$</em>{2}$ system (cm$^{-1}$)</th>
<th>Mode of vibration after laser irradiation in Se$<em>{98}$Ag$</em>{2}$ system (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>537.4</td>
<td>582.1 1024.9</td>
<td>538.0 1024.3 1447.7 1740.9 2854.0 2922.3</td>
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<tr>
<td>1023.8</td>
<td>1024.9 1432.8</td>
<td>1024.3 1447.7 1740.9 2854.0 2922.3</td>
</tr>
<tr>
<td>1383.5</td>
<td>1383.0 1432.8</td>
<td>1266.4 1447.7 1740.9 2854.0 2922.3</td>
</tr>
<tr>
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<td>1456.0 1727.1 2854.0</td>
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</tr>
<tr>
<td>1754.5</td>
<td>1754.5 1727.1 2854.0</td>
<td>1740.9 2854.0 2922.3</td>
</tr>
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<td>2856.0</td>
<td>2856.0 2854.0</td>
<td>2854.0 2922.3</td>
</tr>
<tr>
<td>2924.2</td>
<td>2924.2 2919.1</td>
<td>2922.3</td>
</tr>
</tbody>
</table>

3.3 Micro-hardness analysis

Indenter picture of hardness images are shown in Fig. 12 (a) and (b) for laser exposed and glassy Se$_{98}$Ag$_{2}$ Alloy, respectively. The length scale of diagonals was calibrated and the mean value (average of 10 reading) was used to calculate the micro-hardness ($H_v$). The Indenter is observed for micro hardness at load 100 mg for 15 seconds. The calculated values of micro hardness ($H_v$) by Vickers micro hardness tester and module of elasticity (E) are given in Table 1.

Sanditov [59] proposed a free-volume theory for micro-hardness and gave a equation of microhardness for glasses, based on the energy of micro-void creation, $E_h$ in a volume $V_h$. According to Bartenev [60] the micro hardness is related to the module of elasticity (E) and a Poison’s coefficient, $\mu$, by the

$$H_v = \frac{1 - 2\mu}{6(1 + \mu)} E$$

The obtained value of $\mu$ is 0.25 [61] in case of chalcogenide glasses. One can also obtained the value of module of elasticity (E) as suggested by Boycheva et al [61].

$$E = 15H_v$$

An approximate ratio of hardness ($H_v$) and module of elasticity (E) was calculated from recovered dimensions of hardness indent for the prediction of magnitude [62]. The ratio, of $H_v / E$ is found smaller in case of laser exposed sample. Largest ratio of, $H_v / E$ exhibits the poorest compaction behaviour and high residual stress. Magnitude
of the ratio of, $H_v/E$ suggests the elastic nature of the material during compaction [63].

4. Conclusions

In conclusion, we introduce a simple, quick, and economical laser-stimulated method to synthesize nano-rods consisting of Ag, Se and Ag$_2$Se. This method provides a clean, nontoxic and ecofriendly and efficient route for the synthesis of nano-rods with tunable length and diameter, at room temperature conditions without using any additive. There is no need to use high pressure, energy, temperature, toxic chemicals, downstream processing etc. Handling of the nano-rods is also much easier than other methods. Based on this study, some other nano-rods enclosing Ag$_4$S and Ag$_2$Te phases could be prepared in future. Thus, the present report provides a general and versatile technique to obtain the entire family of silver chalcogenides.

From the point of view of nanotechnology, this is a significant advancement to synthesize silver containing nano-rods.

Further, the structure of Se$_{98}$Ag$_2$ alloy changes significantly after laser irradiation and we have observed strong evidence of crystallization. The activation energy of dc conduction in Se$_{98}$Ag$_2$ alloy faces no significant change significantly after laser irradiation and we have observed a general and versatile technique to obtain the entire family of silver chalcogenides. The activation energy of dc conductivity and optical band gap is responsible for the low values of dc conductivity and optical band gap in case of Se$_{98}$Ag$_2$ alloy. These low values may be due to the shift in Fermi level whose position is determined by the distribution of electrons over the localized states. A Raman spectrum shows the symmetry (E mode) for Se-Se vibrations at the 233 cm$^{-1}$ and 455 cm$^{-1}$ for Se-Ag vibration. FTIR spectra indicate the shifting and rearrangement in term of intense and weak peak after the laser irradiation in Se$_{98}$Ag$_2$ alloy. Micro-hardness $H_v$ and module of elasticity $E$ are slightly increased after the exposure.

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References


[59] D. S. Sanditov Nauka (in Russian), 1974, 236, M.
[60] Bartenev, G. M. Stroizdat, 1974 M.

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