Ultrafast optical nonlinearity in nanostructured selenium allotropes

We synthesized crystalline selenium nanowires and amorphous selenium nanoparticles by a simple chemical route. The morphology and crystalline nature of the samples are studied from XRD and SEM images and optical properties are investigated from UV-Vis absorption spectra and photoluminescence spectra. For nonlinearity studies we used optical excitation in two distinct time regimes: (i) ultrafast excitation using 100 femtosecond laser pulses, and (ii) short-pulse excitation using 5 nanosecond laser pulses. While intensity-dependent, instantaneous nonlinearities are prominent in the ultrafast excitation regime; fluence-dependent, accumulative nonlinearities dominate the short-pulse excitation regime. From z-scan measurements we have calculated the nonlinear absorption coefficients for Se nanostructures. Moreover, we find that these materials are efficient optical limiters with potential applications in laser safety devices.
2.1 Introduction

Selenium (Se) and selenium compounds are known for their ability to form semiconducting quantum dots (QDs) useful for luminescence, photoconductivity and sensing applications. Selenium is also biologically relevant, as it is a trace element found in the human body. It is present in garlic, onion [1] and cow's milk [2]. Using appropriate pump lasers, a number of attractive semiconducting selenium alloys [3], and compounds such as CdSe, PbSe, ZnSe and their quantum dot structures [4-7], have been studied for their nonlinear optical properties. These materials have potential applications in areas like optical switching, signal processing, optical limiting, optical image processing, and laser beam shaping. However, the nonlinear optical transmission of the allotropes of selenium nanostructures has not yet been reported in literature. It would be interesting to investigate the nonlinear behavior of different crystalline forms of the same material as they differ in their electronic, optical and structural properties. For instance, the third-order nonlinear optical susceptibilities of single-crystalline and amorphous 4-butoxy-carbonyl-methyl-urethane polydiacetylene [8] and different polymorphs of oxotitaniumphthalocyanine (TiOPc) [9] measured by third-harmonic generation technique were found to depend significantly on their crystalline structures. Similarly, the structural dependence of third order optical nonlinearity has been studied in tetrathiafulvalene-based molecular corners [10], and a switching over from saturable absorption
to reverse saturable absorption has been reported between an electroactive ligand and its metal complexes [11].

The occurrence of variety of allotropic solid-state forms of selenium can be manifested to its unique position at the boundary of group VI in the periodic table between van der Waals molecular solids (O$_2$ and S$_8$) and covalent solids (Te). Selenium can exist in different allotropic forms including the amorphous state. It consists of a mixture of disordered chains and rings, and five crystalline states including the most stable trigonal and monoclinic forms. Amorphous selenium is thermodynamically unstable, and it transforms easily to stable trigonal selenium under favorable conditions at room temperature. The phase transformation energy from a-Se to t-Se is low at 6.63 kJ/mol.

Extensive investigations of the photoluminescence and the third order optical nonlinearities of nanometer-sized semiconductor materials are progressing, but more interest is to explore the spectroscopic and nonlinear optical properties of different allotropes of the same material. Amorphous selenium as well as trigonal selenium are renowned for their electrical conductivity which is very well enhanced when exposed to light [12-14]. The photoconductivity efficiency is different for these two forms. In view of this, we discuss the synthesis of stable amorphous selenium nanoparticles (a-Se NPs) and trigonal selenium nanowires (t-Se NWs). Their optical nonlinearities are also investigated in the ultrafast (femtosecond) and short-pulse (nanosecond) excitation regimes. The open aperture z-scan technique is used for the measurements, employing 100
fs and 5 ns laser pulses at 800 nm and 532 nm wavelengths, respectively.

2.1.1 Selenium

Selenium is a non-metal discovered by Swedish chemist Jons Jacob Berzelius in 1817 as an elemental residue during the oxidation of sulfur dioxide from copper pyrites in the production of sulfuric acid. It is classified in chalcogen group (group VI A) of the periodic table. Selenium has both metallic and nonmetallic properties and is considered as metalloid. It is positioned between the metals tellurium and polonium and the nonmetals oxygen and sulfur by group and between the metal arsenic and the nonmetal bromine by period.

2.1.2 Applications of Selenium

Selenium is mostly known for its important chemical properties, especially those dealing with electricity. The first photoconductor discovered in 1873 by W. Smith is selenium, while using rods of selenium as resistors to test sub-marine telegraphic cables. He discovered that its resistance depends on whether the resistor is illuminated or not. This property is termed as photoconductivity in which the electrical conductivity of selenium increases due to the
presence of light or in other words, it becomes a better photoconductor as light intensity increases. Because of its photoconductive properties, selenium has applications in photocopying, photocells, solar cells, xerox machines and electrical rectifiers. The selenium solar cell was reported in 1883 by Charles Fritts, and it was available in the market from the 1920s.

2.1.3 Selenium allotropes

![Schematic drawing of the arrangement of Se₈ rings in the α- and β-monoclinic selenium crystals and Se chains in trigonal selenium [15].](image)

Selenium can exist in multiple allotropes that are essentially different molecular forms of an element with varying physical properties.
The most thermodynamically stable allotrope, crystalline hexagonal metallic gray selenium made up of parallel helical chains. The hexagonal unit cell contains three atoms and the lattice parameters at 18 °C are $a = 4.366 \text{ Å}$, $c = 4.954 \text{ Å}$ [16]. The crystalline monoclinic selenium is a deep red and has two forms, labeled $\alpha$ and $\beta$. The Se-$\alpha$ consists of 8-atom non planar rings. The lattice parameters are: $a = 9.054 \text{ Å}$, $b = 9.083 \text{ Å}$, $c = 11.601 \text{ Å}$. The Se-$\beta$ differs from the Se-$\alpha$ in the packing of the rings and lattice parameters are: $a = 12.85 \text{ Å}$, $b = 8.07 \text{ Å}$, $c = 9.31 \text{ Å}$ [16].

Schematic drawing of the arrangement of Se$_8$ - rings in the $\alpha$ - and $\beta$-monoclinic selenium crystals and Se chains in trigonal selenium [15] are shown in Figure 2.1. Another allotrope of selenium is amorphous red powder. It was assumed that a-Se consists of a mixture of rings and chains, with the rings having either 6 or 8 atoms. Though other crystalline phases such as cubic and rhombohedral structures are not common for selenium, the existence of these two phases of selenium is previously reported at normal pressure [16].

### 2.1.4 Se Nanowires and nanoparticles

Nanoparticles (particles of 1-100 nm in diameter) have made intense attention over the past decades because of their unique electronic, optical, photoresponsive, and catalytic properties. In recent years, interest in the synthesis and characterization of nanorods and nanowires has been intensified by their possibility of being used as active components in nanosized devices. Among the amorphous and trigonal forms of selenium, the most widely studied nanostructures [17-22] are a-Se nanoparticles and t-Se nanowires because of the ease of
their growth and formation. During the process of nucleation and growth, amorphous particles usually adopt a spherical shape for minimization of the interfacial free energy. On the other hand the anisotropy in the crystalline structure of trigonal selenium facilitates an easier growth of its 1D nanostructure.

2.2 Experimental

2.2.1 Synthesis of amorphous Se nanoparticles and trigonal Se nanowires

We prepared Se nanostructures by a controlled synthesis route in short reaction time, following a previous chemical method [18] with small changes in the reaction conditions. Selenium powder (0.395g) dissolved in 60ml ethylenediamine, was stirred well and mixed with 40 ml distilled water. The mixture turned brick red in colour indicating the formation of amorphous selenium NPs. a-Se NPs are thermodynamically unstable, and stable solutions can be obtained by adding 0.5 mM PVP in distilled water during the above reaction. On the other hand, if PVP was not added and the mixture is sonicated for 1 hour, the colour slowly turned to black. The resultant black suspension was separated by centrifugation, washed with distilled water and ethanol, and was dried in vacuum to get the end product.

2.2.2 Optical and morphological characterization:

The structural characterizations were done by using Cu-Kα radiation from X-ray diffraction (PANalyticalX′Pert PRO). Elemental analysis was done from Energy dispersive X-ray spectra (JEOL 6390). The morphology of the samples was examined from scanning electron
microscope (SEM) images. The optical spectra of the samples were recorded with UV-Vis spectrometer (Perkin Elmer, Lambda 35) and spectrophotofluorimeter (Fluoromax – 4, Horiba JobinYvon).

2.2.3 Nonlinear transmission experiments:

The z-scan method provides a sensitive and straight forward method for the determination of nonlinear refractive index and the nonlinear absorption coefficient. Using 100 femtosecond laser pulses (FWHM) obtained from a mode-locked Ti:Sapphire laser operating at 800 nm, we measured the ultrafast nonlinear transmission of a-Se NPs and t-Se NWs employing the open aperture z-scan technique [23]. For comparison, short-pulse excitation using 5 nanosecond, 532 nm pulses from a Q-Switched, frequency-doubled Nd:YAG laser was also carried out.

Figure 2.2. Detailed schematic of the z-scan experimental set up
For our nonlinear transmission experiments, we used a plano-convex lens of 20 cm focal length to focus the laser beam. The a-Se and t-Se samples were dispersed in distilled water, and dilutions were adjusted such that when taken in a 1 mm quartz cuvette the linear transmissions were 75% at 800 nm and 60% at 532 nm, respectively. The cuvette is mounted on a stepper motor controlled translation stage which is translated along the focal region of the focused laser beam. By inserting a set of neutral density filters the incident laser pulse energy was set at a suitable value. The incident and transmitted energies as a function of sample position were measured using two pyroelectric laser energy detectors (Rjp735), placed in the far field. The interval between successive laser pulses was kept sufficiently large (about one second) to allow complete thermal relaxation of the excited sample between adjacent laser pulses. The energy meter outputs were digitized with the help of a digital storage oscilloscope, which was interfaced to a PC using the serial port (RS-232). The whole experiment was automated using the LabVIEW software to obtain the z-scan data. A detailed schematic of the experimental setup can be seen in Figure 2.2.

2.3 Results and discussion

2.3.1 Powder X-ray diffraction (XRD)

Figure 2.3 shows the XRD data. While for a-Se NPs the amorphous nature is obvious, for the black suspension all the diffraction peaks measured in the 2θ range are in good agreement with those given in the standard data card for trigonal Se nanowires (ICDDs card No. 06-
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0362). The sharpness of the peaks and absence of impurity peaks assure high crystallinity and purity for the t-Se NWs.

Figure 2.3. XRD spectra of a-Se NPs (I) and t-Se NWs (II).

2.3.2 Scanning electron microscope images (SEM)

The morphology of the t-Se and a-Se samples was studied from scanning electron micrographs (SEM) shown in Figures 2.4(a) and 2.4(b) respectively. Amorphous selenium nanoparticles are spherical and have an average size of 110 nm. Trigonal selenium nanowires grow up to several micrometers in length, and have an average diameter of 120 nm.

Figure 2.5 shows magnified SEM image of t-Se NWs and a-Se NPs. Here, the diameter of t-Se nanowires is found to be comparable with the average size of a-Se nanoparticles. This can be inferred from the growth mechanism involved. Due to the higher free energy of a-Se as compared to t-Se, a-Se colloids slowly dissolve and transform into trigonal phase. Through deposition of dissolved Se, t-Se nanocrystallites
(seeds) grew into uniform, single crystalline nanowires, defined by the lateral dimensions of the nanocrystalline seeds [21].

![Figure 2.4. SEM image of t-Se NWs (a) and a-Se NPs (b)](image)

![Figure 2.5. Magnified SEM image of t-Se NWs (a) and a-Se NPs (b)](image)

### 2.3.3 UV-Visible absorption spectra

UV-Visible absorption spectra (Figure 2.6) reveal that the absorption edge seen in a-Se changes to a broad visible absorption in t-Se, which can be attributed to the crystallization of a-Se into 1-D
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nanowires. a-Se nanoparticles exhibit a semiconducting nature, and the band gap can be determined from the Tauc plot as 2.3 eV (inset of Figure 2.6(a)). For t-Se, absorbance tends to increase with wavelength in the visible spectral region indicating a semi-metallic nature.

![Absorption spectrum of a-Se NPs and t-Se NWs](image)

**Figure 2.6** (a) Absorption spectrum of a-Se NPs. Tauc plot given in the inset gives the bandgap as 2.3 eV. (b) Absorption spectrum of t-Se NWs. Absorbance in the 230-300 nm range is given in the inset.

Earlier workers have reported the electronic density of states, band structure, and charge densities of trigonal and amorphous Se and Te, which can be useful in interpreting physical phenomena observed in these systems [24,25]. Variations in electronic structure with Se nanowire diameter can be studied using first-principles density functional theory (DFT) [26]. The band structure of Se nanowires consists of four principal bands, denoted by VB1 (first valence band), VB2 (second valence band), CB1 (first conduction band) and CB2 (second conduction band). The second valence band is composed of two sub-
bands, namely VB2(a) and VB2(b). For the single shelled Se nanowire of about 1.3 nm diameter, transitions from these sub-bands to the first conduction band occur at 2.38 eV and 4.82 eV respectively. Thinner nanowires result in larger bandgaps. For t-Se NWs, due to structural similarities with the bulk, the properties show a continuous and smooth variation as the size increases towards the bulk regime. Thus for an average wire diameter of 120 nm, different absorption bands in t-Se will become sufficiently broad so as to cause absorption in the entire visible spectral region [22]. It is generally accepted that optical absorption properties of selenium nanostructures depend on the synthesis conditions, microstructure and dimensionality. The measured absorption spectrum of trigonal selenium shows a peak centered at 260 nm and a broad absorption in the visible spectral range. The absorption peak wavelength is close to the values reported for direct transitions in t-Se nanowires [27,28].

2.3.4 Emission spectroscopy

Optical excitation did not yield any photoluminescence (PL) in amorphous Se NPs, but PL was observed in trigonal Se NWs. Excitation at 266 nm resulted in PL emission peaking at 335 nm, confirming electronic transitions between the VB2(a) and CB1 bands [26]. With 350 nm excitation, a weaker emission which peaks at 429 nm was observed (Figure 2.7). These emission maxima are in fair agreement with the values reported for trigonal selenium nanowires prepared through chemical vapour deposition (341.5 nm and 429 nm respectively for 270 nm and 350 nm excitations) [27].
2.7 Photoluminescence spectra measured in t-Se for excitation at 266 nm (I) and 350 nm (II). Corresponding emission peaks are at 335 nm and 429 nm respectively.

2.3.5 Open aperture z-scan curves for fs and ns excitations

The intensity dependent transmissions measured for ultrafast excitations are shown in Figure 2.8 while those for short-pulse excitation are given in Figure 2.9. As discussed below, optical nonlinearity is found to arise from saturable absorption (SA), two-photon absorption (2PA), three-photon absorption (3PA), and excited state absorption (ESA), the relative strengths of which are determined by the excitation regime. While saturable absorption can be inferred from the peaks in the z-scan curves, the dips arise from other processes.
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Figure 2.8. (a) Open aperture z-scan curves measured in a-Se NPs and t-Se NWs for 800 nm, 100 fs excitation, at laser pulse energy of 10 µJ. (b) Nonlinear transmission as a function of input intensity, calculated from the z-scan curves.

Figure 2.9. (a) Open aperture z-scan curves measured in a-Se NPs and t-Se NWs for 532 nm, 5 ns excitation, at laser pulse energy of 90 µJ. (b) Nonlinear transmission as a function of input intensity, calculated from the z-scan curves.

For 100 fs excitation the z-scan of a-Se dispersion shows a single valley, while that of t-Se shows a valley flanked by peaks on either side.
Pure water shows a valley that is shallower. On the other hand, for 5 ns excitation both t-Se and a-Se dispersions exhibit deep valleys, whereas pure water does not show any nonlinearity. In an open aperture z-scan, peaks indicate absorption saturation, while valleys indicate reverse saturation which results in optical limiting. Even though optical nonlinearity is seen in both excitation regimes, the underlying mechanisms are different. For instance, for ultrafast excitation optical limiting occurs mostly due to genuine 2PA/3PA, which is an intensity-dependent instantaneous nonlinearity. On the other hand, for short-pulse excitation optical limiting arises primarily from ESA, involving real excited states, which is a fluence-dependent accumulative nonlinearity. For both ultrafast and short-pulse excitations, a-Se NPs are found to show more efficient optical limiting compared to t-Se NWs.

### 2.3.6 Analysis and fitting of experimental data

For a spatially and temporally Gaussian laser pulse, the input fluence at a given position \( z \) can be obtained from the expression \( F_{\text{in}}(z) = \frac{2E}{\pi \omega^2} \), and the input intensity from \( I_{\text{in}}(z) = \frac{F_{\text{in}}(z)}{\tau} \), where \( E \) is the laser pulse energy, \( \omega \) is the 1/e² beam radius, and \( \tau \) is the 1/e temporal half-width of the pulse [29]. Therefore the z-scan data can be re-plotted in the form of transmission versus input intensity or input fluence, as appropriate for ultrafast or short-pulse excitations. These curves can then be numerically fitted to the relevant nonlinear transmission equations to calculate the nonlinearity parameters. For ultrafast excitation we found that the measured nonlinear transmission fits well
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to a model that includes SA and 3PA/three-step ESA. The corresponding nonlinear absorption coefficient is given by

$$\alpha(I) = \frac{\alpha_0}{1 + \left(\frac{I}{I_s}\right)} + \gamma_{eff}I^2(1)I$$  \hspace{1cm} (2.1)

where $\alpha_0$ is the linear absorption coefficient of the sample, $I_s$ is the saturation intensity, and $I$ is the input intensity. $\gamma_{eff}$ is the effective three-photon absorption coefficient. The corresponding propagation equation is given by

$$\frac{dI}{dz'} = -\left[\left(\frac{\alpha_0}{1 + \left(\frac{I}{I_s}\right)} + \gamma_{eff}I^2\right)\right]I$$  \hspace{1cm} (2.2)

which can be numerically solved to find the best-fit values of $\gamma_{eff}$ and $I_s$. $z'$ is the propagation distance within the sample. Since the role of ESA is minimal for ultrafast excitation, 3PA will be the major contributor to optical limiting in this regime.

The z-scan data for short-pulse excitation is found to fit well to a model in which SA occurs along with ESA/2PA. The nonlinear absorption coefficient for such a case is given by the expression

$$\alpha(I) = \frac{\alpha_0}{1 + \left(\frac{I}{I_s}\right)} + \beta_{eff}I$$  \hspace{1cm} (2.3)

where $\beta_{eff}$ is the effective two-photon absorption coefficient. The propagation equation given by

$$\frac{dI}{dz'} = -\left[\left(\frac{\alpha_0}{1 + \left(\frac{I}{I_s}\right)} + \beta_{eff}I\right)\right]I$$  \hspace{1cm} (2.4)

can be numerically solved, from which the best-fit values of $I_s$ and $\beta_{eff}$ can be found.
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Table 2.1. Nonlinear optical parameters calculated for a-Se and t-Se in water for ultrafast and short-pulse excitations.

<table>
<thead>
<tr>
<th>Material</th>
<th>$I_s$ (×10^16 W/m²)</th>
<th>$\gamma_{eff}$ (×10^31 m³/W²)</th>
<th>$I_s$ (×10^12 W/m²)</th>
<th>$\beta_{eff}$ (×10^10 mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Se</td>
<td>-</td>
<td>3.0</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>t-Se</td>
<td>1.7</td>
<td>0.52</td>
<td>3.5</td>
<td>0.95</td>
</tr>
<tr>
<td>Pure Water</td>
<td>-</td>
<td>0.95</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

From the calculated nonlinear parameters listed in Table 2.1, it can be seen that for ns excitation $\beta_{eff}$ has a relatively high value in the range of $10^{10}$ mW in a-Se as well as t-Se, which is of the same order as that reported for Ag₂Te nanowires measured under similar excitation conditions [30]. For fs excitation $\gamma_{eff}$ is in the order of $10^{-31}$, which is one order of magnitude lower than that reported for ferrofluids under similar excitation conditions [31]. It may be noted here that three-photon absorption at 800 nm (1.55 eV) and two-photon absorption at 532 nm (2.33 eV) are almost identical in terms of photon energy (266 nm, 4.66 eV), and therefore, will excite essentially the same final states in a given molecule.

The nonlinearity shown by a-Se and t-Se as depicted in figures 2.8 and 2.9 can be qualitatively explained on the basis of the relevant electronic transitions. Resonant excitation of a-Se results in the generation of excitons which are relatively long-lived (quadrature frequency resolved spectroscopy (QFRS) studies reveal that the radiative recombination lifetimes of singlet and triplet excitons are ~2x10^-7 s and ~1x10^-4 s, respectively [32]). Therefore optical excitation can lead to
absorption saturation, as well as excited state absorption by self-trapped excitons. Similarly, in t-Se, excitation can induce interband transitions from the second valence sub-band to the first conduction band [26]. Considering the linear absorption spectrum of a-Se, absorption increases progressively for the wavelengths 800 nm, 400 nm and 266 nm, which is conducive to 2PA, 3PA and ESA rather than to SA, when excited either at 800 nm or 532 nm. Therefore a-Se shows an optical limiting action in the range of the input fluencies used. On the other hand, for t-Se absorption increases in the order of 400 nm, 800 nm and 266 nm. This results in absorption saturation at lower fluences for 800 nm excitation, which smoothly gives way to prominent 3PA at higher fluences.

2.4 Conclusions

In conclusion, we have studied the linear and nonlinear optical properties of amorphous selenium nanoparticles and trigonal selenium nanowires synthesized by a simple chemical route. Spectral measurements suggest that a-Se nanoparticles are semiconducting with a band gap of 2.3 eV, and t-Se nanowires are semi-metallic with a broad absorption over the entire visible spectral range. Z-scan studies in the ultrafast and short-pulse excitation regimes reveal saturation as well as reverse saturation of absorption. t-Se nanowires exhibit a tendency for absorption saturation at lower input intensities, due to which its overall optical limiting efficiency is reduced compared to that of a-Se nanoparticles. Nonlinear absorption observed in the ultrafast excitation regime is likely to be dominated by the intensity-dependent three-photon absorption nonlinearity, whereas for short-pulse excitation the major
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contribution may be from the fluence-dependent excited state absorption. From the results obtained it is concluded that Se nanostructures are potential candidates for optical limiting applications, particularly in the short-pulse excitation regime.
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