Ultrafast optical nonlinearity of cubic and amorphous Se doped silica

We investigated ultrafast optical nonlinearity in two different forms of selenium; namely, cubic crystalline and amorphous selenium nanoparticles. Cubic and amorphous Se were doped in silica matrices through so-gel method. The size of the Se semiconductor was calculated from TEM measurements and crystalline nature was examined from SAED pattern. The FTIR spectra of Se doped silica were studied for structural characterizations. The optical absorption spectra were recorded and optical bandgap of both allotropes of Se were calculated. While cubic Se exhibited photoluminescence at 450 nm, no such emission properties were observed for amorphous Se doped silica. The nonlinear optical properties were investigated using the open aperture z-scan, employing 100 fs laser pulses, at 800 nm. Nonlinear absorption observed in the ultrafast excitation regime is likely to be dominated by the intensity-dependent three-photon absorption nonlinearity.
3.1 Introduction

Over last two decades, there has been significant interest in the study of different allotropic forms of materials because of the keenness to explore their fundamental physics and potential applications in a wide range of fields such as photovoltaic devices, biomedical sensing, and nonlinear optics. Different crystalline allotropic phases of carbon have invoked intensive research in recent years due to their extraordinary electrical, thermal, optical and mechanical properties with many intriguing applications [1-5]. Though graphite, diamond, fullerenes, carbon nanotube and graphene were mainly focused to exploit as active components in nanosized devices, selenium allotropes also possess exceptional optical and electronic properties. Selenium exists in different allotropic forms including amorphous form [6], consisting of a mixture of disordered chains and rings. The five crystalline states include monoclinic forms, most stable trigonal form and less reported cubic form. Among them nanostructures of amorphous and trigonal forms of the selenium are most widely studied because of their ease of growth and formation [7-12]. Cubic form exists at normal pressure with unit cell constants $a = 2.97 \text{ Å}$ and $5.755 \text{ Å}$, for $\alpha$ and $\beta$ cubic Se respectively [6]. Even though synthesis of cubic Se is not explored well, $\beta$ cubic selenium nanoparticles were synthesized through biological reduction of $\text{SeO}_3$ using bacteria, Pseudomonas aeruginosa strain J S-11 [13] Biosynthesis of face-centered cubic (fcc) Se nanoparticles having anti DNA damaging property were prepared using lemon plant extract [14].
Selenium and its compounds hold a remarkable position due to their ability in forming semiconducting QDs with fascinating applications in solar cells, xerography and imaging devices [15-17]. They can be incorporated within glasses via the sol-gel process providing fabrication route for developing new class of materials with potential optical and industrial applications. Moreover, selenium based compounds are promising candidates for nonlinear optical applications including ultrafast and short pulse excitations. Optical nonlinearity of the allotropes of selenium nanostructures – amorphous selenium nanoparticles and trigonal selenium nanowires were recently studied in femtosecond to nanosecond time scales [18]. The incorporation of semiconductor nanocrystallites in strained glassy host matrices is helpful in avoiding degradation and improving their stability for nonlinear optical applications with large optical nonlinearities and fast response. Homogeneously and individually dispersed multiwalled carbon nanotube (MWCNT) in silica demonstrated sustained nonlinear optical properties at both 532 and 1064 nm laser wavelengths [19]. Also, through the introduction of Cu$_{7.2}$S$_4$ quantum dots, an enhancement in third-order nonlinear properties of sodium borosilicate glass was measured using z-scan technique with femtosecond excitations [20].

In this chapter, we discuss the synthesis of cubic and amorphous Se nanoparticles through sol-gel route. Other than the biological production of cubic Se by bacteria, to our knowledge no studies have been reported on the chemical synthesis and characterization of cubic Se nanocrystallites. Their structural, crystalline and optical properties are investigated in detail and nonlinear transmissions with ultrafast
excitations at 800 nm are studied using the open aperture Z-scan technique.

### 3.1.1 Sol-gel process

The sol-gel process may be described as “formation of an oxide network through polycondensation reaction of a molecular precursor in liquid”. The sol-gel process is a wet chemical technique used for the fabrication of both glassy and ceramic materials. Alkoxides are ideal chemical precursors for sol-gel synthesis because they react readily with water.

Figure 3.1 shows processing steps of sol-gel processing to prepare sol-gel derived silica monoliths. The most commonly used precursor materials for the silica sol formation are tetramethylorthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) which are mixed with alcohol, water, a co-solvent, and an acid or base catalyst at room temperature (Figure 3.2).
A sol-gel process occurs in several steps:

- Hydrolysis and condensation: formation of sol
- Gelation: sol-gel transformation
- Ageing: crack resistant stiff gel
- Drying: aerogel/xerogel

The basic chemical reactions are as shown below. First step is hydrolysis of the alkoxide precursor.

\[
\begin{align*}
\text{Si} \ (OR)_4 + H_2O & \rightarrow \text{HO-Si} \ (OR)_3 + \text{R(OH)} \\
\text{Si} \ (OR)_4 + 4H_2O & \rightarrow \text{Si(OH)}_4 + 4\text{R(OH)}
\end{align*}
\]

R is an alkyl group and R(OH) is an alcohol. Depending on the amount of water and catalysts present, hydrolysis may go to completion or stop while it is only partially hydrolysed, Si(OR)_{4-n}(OH)_n.
Two partially hydrolysed molecules can link together in a condensation reaction such as,

\[(\text{OR})_3\text{-Si-OH} + \text{OH-Si-(OR)}_3 \rightarrow (\text{OR})_3\text{-Si-O-Si-(OR)}_3 + \text{H}_2\text{O}\]

Or

\[(\text{OR})_3\text{Si-OR} + \text{OH-Si (OR)}_3 \rightarrow (\text{OR})_3\text{Si-O-Si (OR)}_3 + \text{R-OH}\]

The above reactions of a sol-gel system undergoing concurrent hydrolysis and condensation can be summarized as

\[n\text{Si(OR)}_4 + 4n\text{H}_2\text{O} \rightarrow n\text{Si(OH)}_4 + 4n\text{ROH}\]

\[n\text{Si(OH)}_4 \Rightarrow 3n\text{SiO}_2 + 2n\text{H}_2\text{O}\]

As this condensation reaction grows, more and more Si-O-Si bonds are formed and may be steered in the desired direction by adjusting the proper parameters. The parameters which influence condensation are

- Type of precursors
- The ratio between alkoxide and water
- Type of catalyst used
- Type of solvent
- Temperature and PH
- Relative and absolute concentration of reactants

A gel is a stiff mass of a continuous phase, more like a viscous liquid. Gelation occurs when the growing polymers cross-link to form an extensive three-dimensional network. Gelation results in the form of a solid in the shape of the mold. Aging of a gel also called syneresis involves maintaining the cast object for a period of time, hours to days.
completely insulated from the surroundings. An aged gel must develop sufficient strength to resist cracking during drying. Drying is the process that consists of eliminating the interstitial liquid phase due to capillary forces that actively transport the liquid to the surface for evaporation. Usually two methods of drying are used for the removal of solvents from gel monoliths. While drying by slow rate of evaporation of solvents at normal atmospheric pressure results dried gel called xerogel, drying the wet gel under super critical condition gives the product known as aerogel.

3.2 Experimental

3.2.1 Synthesis of cubic Se and amorphous Se doped silica matrices

Silica glasses with 10 wt% Se were prepared by sol-gel process with tetraethyl orthosilicate (TEOS), as precursor in the presence of ethanol and doubly distilled water. A measured volume of 1M HNO\(_3\) was added as catalyst. The TEOS/H\(_2\)O/HNO\(_3\) molar ratio was 1:12:0.01. Se nanocrystallites were prepared by the decomposition reaction of selenous acid and were incorporated on to the SiO\(_2\) matrix through annealing. Appropriate amount of selenous acid dissolved in doubly distilled water and ethanol was poured into TEOS under stirring at room temperature. The resulting mixture was stirred continuously for about an hour at room temperature till it formed a uniform clear solution. The mixture (sol) poured into polypropylene containers was sealed and kept to form stiff gel for one month.
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Samples were then heated in a hot air oven at 60 °C for three day to eliminate organics and water present. Finally the samples were annealed at 200 °C with a rate of heating 30 °C/hr in a programmable furnace for two hours. The color of the xerogel turned into deep orange upon heating. The compositions of the prepared samples are summarized in Table 3.1. A photograph of Se doped sample is shown in Figure 3.3.

**Table 3.1 Compositions of the prepared samples**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>wt% of Se</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10%</td>
<td>200 °C</td>
</tr>
<tr>
<td>B</td>
<td>10%</td>
<td>60 °C</td>
</tr>
</tbody>
</table>

![Photograph of Se doped sample heated at 200 °C (a) and 60 °C (b)](image)

**3.2.2 Optical and morphological characterization**

The morphological and crystalline nature of the nanoparticles were evaluated from transmission electron micrographs (TEM) and selected area electron diffraction (SAED) patterns of the samples obtained on J EM 2100 electron microscope. Elemental analysis was done from the energy dispersive X-ray (EDX) spectra obtained from scanning electron microscope J EOL J SM 6390. The FTIR spectra of the samples in
the region 400-4000 cm\(^{-1}\) were recorded by using Shimadzu FTIR spectrometer 8400 S for structural analysis. The UV-Visible absorption and emission spectra of the samples measured with UV-visible spectrophotometer (Shimadzu-UVPC2401) and spectrofluorophotometer (Fluoromax – 4 - Horiba Jobin Yvon) respectively were used for optical characterization.

3.2.3 Experimental measurement of nonlinear transmission

The fluence-dependent nonlinear optical transmission of c-Se and a-Se doped silica was measured from open aperture Z-scan [21] experiments. For the open aperture z-scan experiments 100 fs laser pulses at 800 nm wavelength from a Ti:Sapphire laser was used as the excitation source. Samples were loaded as such on a programmable linear translation stage and were scanned along the beam axis through the beam focus. A set of neutral density filters were used to set the incident laser pulse energy to a suitable value. The laser pulses were focused using a converging lens so that sample experiences different laser intensities at each point with maximum intensity at the focus. The incident and transmitted energies at every point were measured using pyroelectric laser energy detectors. The experiment was automated using a LabVIEW program.

3.3 Results and discussion.

3.3.1 Transmission electron micrographs (TEM)

Crystalline structure and morphology of Se doped silica was examined from SAED patterns (Figure 3.4) and TEM (Figure 3.5 (a) and 3.6(a)). For sample A the SAED pattern clearly shows the amorphous
nature of the sample. The prominent rings in the SAED pattern of sample B can be indexed to pure cubic structure (ICDD No. 38-0768). The d-spacings obtained as 3.065 Å, 1.942 Å, and 1.669 Å, 1.3513 Å, 1.235 Å, 1.043 Å are consistent with the (100), (110), (111), (210), (211), and (300) lattice planes of the cubic phase of Se. The uniform nanometer-sized particles ranging from 4 - 8 nm and 3 - 6 nm is measured from the TEM image (Figure 3.5 (a), 3.6 (a)) for a-Se and c-Se respectively.

Figure 3.4 SAED pattern of cubic (a) and amorphous (b) Se doped Silica

Figure 3.5 (b) shows HRTEM image of amorphous Se doped silica which does not contain any fringe spacings confirming the formation of amorphous phase. The HRTEM of cubic Se (Figure 3.6 (b)) reveals a high crystallinity with well resolved lattice fringes throughout the whole particle with a d-spacing of 3.016 Å which can be assigned to (100) plane of cubic Se. Correspondingly, the fast Fourier transform (FFT) of the image shown in Figure 3.6 is in almost perfect agreement with the
calculated diffraction pattern of the cubic Se structure, aligned along the (100) plane of cubic Se with a d-spacing of 2.991 Å.

Figure 3.5 TEM (a) and HRTEM (b) of amorphous Se doped Silica

Figure 3.6 TEM (a) and HRTEM (b) of cubic Se doped Silica. FFT pattern of lattice planes in HRTEM is given in the inset.
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A more detailed analysis on inter planar spacing is done from image processing applied to the magnified image using surface plot analysis generated from ImageJ software. The surface plot obtained by selecting a square area of parallel lattice fringes in the magnified image is shown in Figure 3.7. The interplanar distance of (100) plane obtained from the ratio of distance and number of peaks is compared with those obtained from HRTEM and SAED pattern (Table 3.2).

![Surface plot obtained from HRTEM of c-Se](image)

**Figure 3.7 Surface plot obtained from HRTEM of c-Se**

<table>
<thead>
<tr>
<th>d_{SAED} (Å)</th>
<th>d_{HRTEM} (Å)</th>
<th>d_{FFT} (Å)</th>
<th>d_{surface plot} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.065</td>
<td>3.016</td>
<td>2.991</td>
<td>3.034</td>
</tr>
</tbody>
</table>

### 3.3.2 Energy dispersive X-ray spectroscopy (EDX)

To further identify the chemical composition of the particles, we used EDX spectroscopy which clearly indicates that Se doped silica sample is composed of Si, O and Se as expected. Both c-Se and a-Se
gave similar EDS spectra and the spectrum of pure silica is given for reference (Figure 3.8).

![Figure 3.8 EDX spectra of silica (a) c-Se (b) and a-Se (c) doped silica](image)

**Figure 3.8 EDX spectra of silica (a) c-Se (b) and a-Se (c) doped silica**

### 3.3.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of Se doped silica glass dried at 60 °C and 200 °C are shown in figure 3.9. The FTIR spectra of Se nanoparticles embedded silica glass are similar to the spectrum of pure SiO$_2$ [22] with strong...
bands associated with Si-O stretching and bending vibrations. These bands are observed at 799 and 1057 cm\(^{-1}\). The broad absorption around 3325 cm\(^{-1}\) indicates the presence of water (hydroxyl group). For a-Se doped silica, the bands due to the presence of absorbed water decrease in intensity due to the increase in annealing temperature. Moreover, weak absorption at 1645 and 965 cm\(^{-1}\) indicate the presence of oxyethyl group which decreases with heat treatment. This indicates the gradual strengthening of silica network through cross-linking.

![Figure 3.9 FTIR spectra of c-Se and a-Se doped silica.](image)

### 3.3.4 UV-Visible absorption spectra

Optical excitation of electrons across the band gap is strongly permitted, producing an abrupt increase in absorption at the wavelength corresponding to the gap energy. This feature in the optical spectrum is known as the absorption edge. The absorption spectra corresponding to
the Se doped silica glass dried at 60 °C and 200 °C is shown in Figure 3.10. The direct absorption bandgap of the semiconductor nanoparticles can be determined from the equation

\[ \alpha h\nu = B(h\nu - E_g)^{1/2} \]  

(3.1)

in which \( h\nu \) is the photon energy, \( \alpha \) is the absorption coefficient, \( E_g \) is the absorption bandgap and \( B \) is a constant relative to the material. The absorption coefficient can be obtained from the equation

\[ \alpha = \frac{2.303A}{d} \]  

(3.2)

where \( A \) is the absorbance and \( d \) is the thickness of the sample. The plot of (3.2) versus \( h\nu \) [inset of Figure 3.10], gives the value of the bandgap as 3.5 eV and 2.4 eV for c-Se and a-Se respectively.

The calculated band gap for a-Se doped silica is comparable with that of the reported values [18]. Also, the band gap energy is blue-shifted relative to the bulk band gap due to the quantum size effect. However, the band structures of the cubic form have not been investigated in detail. Observed absorption spectrum is similar to that obtained for fcc Se nanoparticles with an absorption maximum at 395 nm [14]. As trigonal structure of Se is closely related to simple cubic structure, with just a small trigonal distortion, band to band transitions in cubic form can be approximated to that of trigonal structure [23]. For trigonal Se, the first excitonic peak is associated with direct transitions at 1.95 eV.
and second excitonic peak is associated with band edge transition at 3.09 eV [24]. Hence the observed band gap 3.5 eV for cubic Se due to exciton absorption can be considered blue shifted due to the quantum confinement.

![Absorption spectra of c-Se (a) and a-Se (b) doped silica. Tauc plot given in the inset gives the bandgap as 3.5 eV and 2.4 eV.](image)

**Figure 3.10.** Absorption spectra of c-Se (a) and a-Se (b) doped silica. Tauc plot given in the inset gives the bandgap as 3.5 eV and 2.4 eV.

### 3.4 Emission spectrum

Photoluminescence spectrum of c-Se doped silica at an excitation of 340 nm wavelength is shown in Figure 3.11. For a-Se doped silica no emission was observed, which is in agreement with the studies explained in chapter 2. For trigonal Se nanowires, excitation at 266 nm and 350 nm resulted in PL emission peaking at 335 nm and 429 nm respectively [18]. As only amorphous and trigonal form of selenium is widely studied, reports on photoluminescence in cubic form are rarely seen. Moreover, calculations of the band structure, density of states, and charge densities for cubic form of Se are not studied widely. Hence the optical transition
behind the observed emission band could not be fully explained. As the band gap obtained for c-Se is 3.5 eV, the emission band observed at an excitation of 3.6 eV is band edge emission. Similar band edge emission was observed in fcc selenium nanoparticles synthesized using leaf extract where an emission peak was observed at 525 nm with 395 nm excitation [14].

![Emission spectrum of c-Se doped Silica](image)

**Figure 3.11. Emission spectrum of c-Se doped Silica**

### 3.4.1 Nonlinear transmission in c-Se and a-Se doped silica

The nonlinear absorptive changes in a material induced by a strong beam of light can be measured by the z-scan technique. The intensity dependent nonlinear transmissions measured for ultrafast excitation are shown in Figure 3.12. Samples used have a linear transmittance of 85% at the excitation wavelength of 800 nm. The open aperture z-scan curves exhibit valleys indicating reverse saturable
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absorption with a-Se doped silica exhibiting deep valleys. For c-Se doped silica the z-scan curves looks similar with that of pure silica. The nonlinear transmission as a function of input intensity is plotted in Figure 3.12 (b,d) and optical limiting efficiency is found to be enhanced for a-Se doped silica matrix.

Figure 3.12. Open aperture Z-scan curves measured in a-Se doped silica matrix (a) and c-Se silica doped silica matrix (c) for 800 nm, 100 fs excitation, at laser pulse energy of 10 µJ. Nonlinear transmission as a function of input intensity, calculated from corresponding z-scan curves (b),(d).
3.4.2 Analysis and fitting of experimental data

For ultrafast excitation the nonlinear absorption occurs mostly due to genuine 2PA/3PA involving simultaneous absorption of two or more photons. To understand the mechanism behind this intensity-dependent instantaneous nonlinearity, the experimental z-scan curves are numerically fitted to the relevant nonlinear transmission equations. For pure silica matrix and c-Se doped silica, we found that the obtained nonlinear transmission data fit well to a model in which SA occurs along with ESA/2PA. The nonlinear absorption coefficient is given by the expression

\[ \alpha(I) = \frac{\alpha_0}{1 + (\frac{I}{I_s})} + \beta_{eff} I \]  

(3.3)

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

\[ \frac{dI}{dz} = -[\alpha_0 / (1 + (I / I_s)) + \beta_{eff} I]I \]  

(3.4)

can be numerically solved, from which the best-fit values of \( I_s \) and \( \beta_{eff} \) can be found. \( z' \) is the propagation distance within the sample.

The best fit for nonlinear absorption in a-Se silica is obtained by a model that includes 3PA in addition to 2PA and saturable absorption. The corresponding propagation equation is given by
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\[
\frac{dI}{dz} = -\left[\left(\alpha_o/1 + \left(\frac{I}{I_s}\right)\right) + \beta_{\text{eff}} I + \gamma I^2\right] I
\]

The calculated nonlinear parameters are listed in Table 3.3. It can be seen that addition of cubic Se to silica exhibits no modification in the nonlinear optical parameters of pure silica. Even if cubic selenium could not behave as a nonlinear material with ultrafast excitations, amorphous selenium could contribute to ultrafast optical nonlinearity through three photon absorption phenomenon. The value of \(\gamma_{\text{eff}}\) is in better agreement with those reported for amorphous Se under similar excitation conditions [18]. From the input intensity dependent normalized transmittance measurements it is clear that the transmittance remains the same at low input intensity and then decreases as the intensity increases. This typical feature indicates that silica and a-Se doped silica are potential optical limiting candidates. A quantitative comparison shows that the optical limiting threshold of a-Se doped silica is 0.54 J/cm\(^2\) which is better than those previously reported for C\(_{60}\) (2 J/cm\(^2\)) [25] and comparable with graphene nanosheets (0.5 J/cm\(^2\)) [26].

**Table 3.3. Nonlinear optical parameters calculated for a-Se and t-Se for ultrafast and short-pulse excitations.**

<table>
<thead>
<tr>
<th>Material</th>
<th>(I_s) ((\times 10^{15}\text{W/m}^2))</th>
<th>(\beta_{\text{eff}}) ((\times 10^{-15}\text{m/W}))</th>
<th>(\gamma_{\text{eff}}) ((\times 10^{-31}\text{m}^3/\text{W}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 fs, SiO(_2)</td>
<td>5.5</td>
<td>4.8</td>
<td>-</td>
</tr>
<tr>
<td>800 nm c-Se – SiO(_2)</td>
<td>5.4</td>
<td>4.8</td>
<td>-</td>
</tr>
<tr>
<td>excitation a-Se – SiO(_2)</td>
<td>5.4</td>
<td>4.9</td>
<td>3.4</td>
</tr>
</tbody>
</table>

99
For a-Se doped silica the observed optical nonlinearity may have contributions from genuine three photon absorption as well as two photon induced free carrier absorption process. As the band gap is calculated as 2.4 eV, it can be inferred that the excitations at 1.55 eV can lead to simultaneous absorption of two photon to higher energy levels in the conduction band. This is followed by further free carrier absorption from the conduction band. Thus the nonlinear absorption coefficient can be considered as an effective three photon absorption which arises from two photon absorption followed by excited state absorption. Nonlinear optical transmission in Zn\textsubscript{1-x}Mg\textsubscript{x}O thin films examined using ultrafast excitations at 800 nm has previously been reported to be due to three photon induced free carrier absorption [27]. Hence the improved optical limiting property measured for a-Se doped silica gives way for developing glasses which inhibit intense laser beam thereby protecting the optical sensors.

3.5 Conclusions

Silica xerogels doped with cubic and amorphous Se were prepared through sol-gel route. The structural properties of silica xerogels are investigated in detail from FTIR spectroscopy. The optical properties of cubic and amorphous phases of selenium nanoparticles are studied from UV-Vis absorption measurements over the entire visible spectral range and photoluminescence spectra. The average size of the nanoparticle estimated from the TEM images while the crystalline nature of the nanoparticles are examined from SAED pattern. The crystalline cubic structure is confirmed from HRTEM image which clearly shows lattice
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fringes with randomly oriented nanocrystallites. Ultrafast optical nonlinearity of amorphous Se doped xerogel glasses investigated from z-scan technique reveals an improved nonlinear absorption at 800 nm excitation. Interestingly no such enhancement was observed for cubic Se doped glasses. The optical nonlinearity is found to be dominated by genuine three photon absorption with contributions from two photon induced free carrier absorption process. These intensity-dependent, instantaneous nonlinearities with fast response make them attractive candidates for ultrafast optical limiters.
Chapter 3

References
