Among the well studied semiconducting nanomaterials, transition metal chalcogenides own a renowned position which includes elemental semiconductor Se and IB-VIA metal sulfides (Ag$_2$S, CuS). General introduction on chalcogenide based materials are presented along with a brief review on Se nanostructures, Ag$_2$S and CuS nanoparticles, semiconductor- semiconductor nanocomposites and alloys. A short discussion on synthesis, growth and defects of nanomaterials is also given. In addition, general introduction to the nonlinear optical properties of matter in a strong laser field is detailed. A detailed description of various nonlinear absorption processes and applications of nonlinear absorption in designing optical limiters is also included. An overview of the generation of ultrafast laser pulses and experimental technique for nonlinear transmission measurements is also mentioned. Evolution of optical nonlinearity from nanosecond to femtosecond excitation domains is briefly described. The organization of the thesis, the aim and objective of the research work are also touched upon at the end of the chapter.
1.1 Chalcogen based nanosemiconductors

The growing interest in nanostructured materials calls for the development of processing techniques that allow tailoring of specific features of nanometer size. Semiconductor nanoparticles have received significant attention for the past decades and considerable progress has been achieved in the areas of synthesis, structural characterization, electronic and optical properties of semiconductor quantum dots (QDs) [1-4]. The interests are technological, for eventual applications in solar energy conversion, optoelectronic devices, molecular and cellular imaging, and sensitive photodetectors or purely fundamental because of the specific properties of these materials [5-10]. Materials based on group VI elements are generally termed as chalcogenide compounds and semiconducting chalcogenide binary compounds include oxides, sulfides, selenides and tellurides of metals like Cd, Zn, Pb, Ag, Cu etc. Earlier research works were mostly devoted on developing nanoparticles of II-VI and III-V semiconductors. By comparison, little scientific studies have been done with I-VI semiconductor materials such as Ag$_2$S and CuS. Moreover, elemental semiconductor Se is quite exciting and interesting candidate due to its ability to form variety of allotropic forms.

Different architectures are achievable for semiconductor nanomaterials such as quantum well (one dimensional confinement), quantum wire (two dimensional confinement) and finally quantum dots (three dimensional confinement). The spatial confinement of the charge carriers in a semiconductor nanocrystal can occur in different directions depending on the dimensions and shape of the nanocrystal and the extension of the electron and hole wave functions. A major feature of
Chapter 1

The semiconductor quantum dots (QDs) is the quantum confinement effect, which leads to spatial enclosure of the electronic charge carriers within the nanocrystal. Because of this effect, we can use the size and shape of these “artificial atoms” to tune the energy of optical transitions. This phenomenon is known as quantum size effect [11]. As QD size decreases, the energy gap increases, leading to a blue shift of emission wavelength. Quantum confinement essentially leads to a collapse of continuous energy bands of the bulk material into discrete “atomic” energy levels. As a result, they have superior transport and optical properties. In particular, they have size tunable optical absorption and narrow and intense photoluminescence spectral features. They have gained considerable attention in recent years because they possess high optical nonlinearities. They can be used in diode lasers, amplifiers and biological sensors.

1.1.1 Review on Se nanostructures

In 1873 Willoughby Smith noticed the photoconductivity of selenium. Later in 1876 William Grylls Adams and Richard Evans Day discovered that selenium produces electricity when exposed to light [12]. Although selenium solar cells fail to convert enough sunlight to power electrical equipment, they proved that a solid material can generate electricity from light, without thermal or mechanical energy. In the past few years, a number of methods have been demonstrated for making of Se nanomaterials including amorphous and trigonal nanostructures.

Gautam and coworkers successfully reported preparation of trigonal Se (t-Se) nanowires and nanorods through decomposition of
General Introduction

\[(\text{CH}_3\text{N})_4\text{GeSe}_{10}\] and reaction of selenium powder with NaBH\(_4\) [13]. Tang and his co-workers synthesised single crystalline Se microtubes through decomposition of Na\(_2\)SeSO\(_3\) using H\(_2\)O\(_2\) as a reducing agent [14]. Protein cytochrome C\(_3\) has been used to make selenium nanowires for the formation of amorphous Se (a-Se) by Abdelouas et al [15]. L-Cystine has been employed as a reducing agent as well as a soft template by Chen et al. to manage the growth of Se nanorods [16]. Xie and co-workers used direct vapor deposition process to synthesize Se nanoribbons [17]. Zhu et al. produced Se nanowires and nanorods from SeO\(_2\) through a microwave polyol route [18]. Ren et al. prepared Se nanowires from a physical transportation method with Si as co-source material [19]. Wang et al. synthesized Se nanorod bundles with sodium selenosulphite as a selenium source and polyvinyl alcohol as polymer [20]. Xia and co-workers worked on the generation of 1D Se nanostructures in the presence of hydrazine monohydrate as the reducing agent [21,22]. Particularly, Fan et al. prepared Se microrods and microtubes with Se powder and NaOH as precursors under hydrothermal conditions [23]. A simple wet chemical method for the synthesis of PVA stabilized selenium nanoparticles from sodium selenosulphate precursor was also reported [24]. Amorphous Se nanospheres were prepared with Na\(_2\)SeSO\(_3\) as Se source by altering the pH of the solution [25]. Trigonal Se nanowires were obtained in water at room temperature by Qing et al. using ascorbic acid as reducing agent under the assistance of β-cyclodextrin [26].

In addition to amorphous and trigonal forms of selenium, α-phase monoclinic selenium and β-phase monodinic selenium were reported.
The spontaneous transformation of monoclinic Se micro-balls to nanorods having trigonal crystal phase was observed in a glow discharge set-up [28]. Even though synthesis of cubic Se is not explored well, cubic selenium nanoparticles were synthesized through biological reduction of SeO$_3$ using bacteria, Pseudomonas aeruginosa strain JS-11 [29].

1.1.2 Review on Ag$_2$S nanoparticles

Ag$_2$S has band gap energy of 0.9 eV fulfilling the demand for near infrared (NIR) emitting quantum dots (NIRQDs), especially in biological applications and for photovoltaic applications. Ag$_2$S is stable in its α-monoclinic crystal phase (α-Ag$_2$S, acanthite type, space group P2$_1$/n) and several reports on Ag$_2$S nanocrystals have been published. Wang and co-workers prepared single-crystalline monodisperse Ag$_2$S nanoparticles with an average size of about 10 nm through a single source precursor route, and the NIR emission at 1058 nm was first observed [30]. Later, monodisperse Ag$_2$S nanocrystals with a size of about 5 nm were synthesized by Li. et al. [31]. Monodisperse metal sulfide nanocrystals (NCs) including Ag$_2$S NCs were developed in organic non polar solutions using (NH$_4$)$_2$S as a sulfide precursor [32]. A one-step synthesis method was developed by Acar et. al to prepare 2-mercaptopropionic acid (2-MPA) coated aqueous Ag$_2$S NIRQDs and the cytocompatibility of the particles was investigated [33]. Also water soluble Ag$_2$S quantum dots with tunable emissions were synthesized through a one-step method and in vivo imaging was performed to investigate their potential applications for biomedical labeling [34]. Wang et al. prepared silver sulfide (Ag$_2$S) nanoparticles using a one-pot route using silver acetate and n-
dodecanethiol as raw materials [35]. Silver sulfide nanoparticles were synthesized using a simple aqueous precipitation using different stabilizing agents to control particle size and agglomeration [36]. Hexagonal nanosized Ag₂S was prepared in the presence of PVP (polyvinylpyrrolidone) through complex formation with ethylenediamine at room temperature [37].

For past few years, several approaches, such as the solvothermal method [38], single-source precursor routes [39], the laser ablation method [40] and so on, have been recently documented in the literature for the synthesis of Ag₂S nanoparticles. Through the solvothermal or hydrothermal route, the shape and size of the nanoparticles could not be efficiently controlled. Also, the single-source precursor synthetic method mentioned above is not applicable for the large-scale synthesis of high-quality nanoparticles. Moreover, deposition of nanomaterials over a large area and reproducibility is not easy for the laser ablation method. Hence, it remains a challenge to build up an uncomplicated and inexpensive approach, for large scale synthesis of Ag₂S nanoparticles. Although there are many literatures available on Ag₂S nanoparticles, a simple and cost effective method to synthesize water dispersible Ag₂S nanoparticles is receiving tremendous demand in recent years.

1.1.3 Review on CuS nanoparticles

Copper sulfide can exist in a wide range of stoichiometries ranging from the 'copper rich' Cu₂S to 'copper deficient' CuS₂ including five stable phases at room temperature, such as covellite CuS, anilite Cu₁.75S, digenite Cu₁.8S, djurleite Cu₁.95S, and chalcocite Cu₂S with a
tunable bandgap from 1.2 to 2.0 eV. CuS shows p-type semiconductor or metallic conductivity and transforms into a superconductor at 1.6 K. Toward this end, considerable efforts have been devoted on preparing copper sulfide nanocrystals having different phases with specific morphologies and architectures. For example, Korgel et al. prepared nanorods, nanodisks, and nanoplatelets of Cu$_2$S from a single source precursor, copper alkylthiolate through a solventless synthetic technique [41,42]. Digenite nanowires and djurleite nanotubes were fabricated from CuCl and thiourea through a hydrothermal method [43]. Chen et al. reported a thermal decomposition method using [Cu(acac)$_2$] and sulfur in oleylamine to synthesize monodisperse Cu$_2$S nanoplates [44] and nanoflakes of CuS [45]. Moreover, CuS nanoplatelets and hierarchical doughnut-shaped CuS particles were prepared from a solvothermal method in toluene with hexadecylamine as a capping agent [46]. In addition to several reports on copper sulfide nanostructures with various morphologies, there are several reports on monodisperse copper sulfide nanocrystals. Nanocrystals of Cu$_9$S$_8$, Cu$_7$S$_4$ and CuS were developed in autoclaves using [Cu(NH$_3$)$_4$]$^{2+}$ and thiourea in sealed autoclaves and possible mechanism of phase transformation among copper sulfides was discussed by Xie et al. [47]. Sathyamoorthy et al. reported a low temperature growth of CuS nanoparticles by reflux condensation method [48]. By using copper acetate monohydrate and thiourea as precursors, a stable colloidal dispersion of (CuS) nanoparticles in water was prepared with SDS, PVP and Na-AOT as stabilizing agents [49]. Recently, through a typical hot-injection method using CuCl and S powder as precursors, controllable transformation
from rhombohedral Cu$_{1.8}$S nanocrystals to hexagonal CuS clusters was reported [50]. Moreover, CuS nanoparticles synthesized by wet chemistry revealed their potential application in photothermal ablation of tumor cells and are promising materials for treatment of cancer [51]. Zhu et al. prepared oleic acid-modified CuS nanoparticles through a surface modification technique in absolute alcohol-distilled water mixed solution [52]. CuS nanoparticles were prepared by Dong et al. in water-in-carbon dioxide microemulsion from Cu(NO$_3$)$_2$ and Na$_2$S [53]. Haram et al. used copper ammonia complex and thiourea as starting materials to synthesize CuS nanoparticles in Triton-X 100/cyclohexane water-in-oil microemulsions [54]. Using a simple colloidal route water soluble covellite CuS quantum dots were prepared through a colloidal method with alanine as the stabilizing agent [55].

Though many methods have been developed for preparing CuS nanocrystals, most of these synthetic methods involve template or complex equipment and high temperature treatment. Hence, it still remains a challenging task to design and develop novel, green, facile, low temperature and simple solution-based methods to synthesize water dispersible CuS nanoparticles and quantum dots.

**1.1.4 Review on semiconductor-semiconductor nanocomposites**

Semiconductor nanoparticles (NPs) are highly useful because of their tunable band gaps arising from confinement effects, but semiconductor-semiconductor nanocomposites (NCs) are even more advantageous since their optoelectronic properties can be tuned additionally by varying the constituent nanocrystal stoichiometries.
From past several years immense interest have been devoted on chalcogen based nanocomposites to explore their optical and nonlinear optical properties. Wang et al. developed PbS/ZnO nanocomposite films of optical quality with a sol-gel method and a large refractive nonlinearity was observed [56]. Also Panda et al. prepared CdS–ZnO nanocomposite thin films using the sol-gel technique and composite films were deposited by the spin coating technique [57]. One-Pot synthesis of highly fluorescent Fe$_2$O$_3$–CdSe nanocomposites using cadmium stearate (Cd(St)$_2$) and iron stearate (Fe(St)$_2$) as precursors were also reported [58]. Through a sonochemical route, Liu et al. presented a method to prepare Fe$_3$O$_4$/CdS nanocomposites in aqueous solution [59]. Recently, a rapid microwave-assisted synthesis for making Fe$_3$O$_4$/CdSe magnetic/luminescent nanocomposites was performed by Zedan et al. where luminescent CdSe nanoshells are grown around magnetic Fe$_3$O$_4$ nanocrystalline seeds [60]. A composite of Ag$_2$S-TiO$_2$ nanoparticles and Ag$_2$S coupled TiO$_2$ nanowires were prepared by Xie et al. exhibiting high visible-light-induced catalytic activity [61]. CdO-CdS nanocomposites are also known to have enhanced photocatalytic activity and can be applicable for hydrogen generation from water [62]. The spectral and nonlinear optical properties of ZnO-Ag [63], ZnO-CdS [64], ZnO-TiO$_2$ [65] and ZnO-TiO$_2$-SiO$_2$ [66] nanocomposites were prepared through colloidal chemical synthesis.

1.2 Synthesis and growth of nanocrystals

The formation of the nanocrystals involves nucleation of an initial ‘seed’, and further chemical growth of nanometer-sized materials. This
can be achieved by carefully controlling the parameters for particle formation from a single solution or mixture of solution. In the nucleation step, precursors decompose or react at a relatively high temperature resulting in a supersaturated solution followed by nucleation of nanocrystals. These nuclei undergo subsequent growth by consuming additional monomers (Figure 1.1).

Figure 1.1. The stages of nucleation and growth of nanocrystals in the framework of the La Mer model [67]

So far several methods have been reported for the synthesis of semiconductor nanocrystals or quantum dots. Some of the major methods used to prepare semiconductor nanocrystals are explained in this section. Colloidal synthesis involves chemical reactions in solution at a particular temperature to prepare semiconductor nanostructures of different composition, size and shape. In addition to temperature and
concentration of the precursors, the formation of nanocrystals depends on precursors, solvents and surfactants used for the synthesis. Rapid addition of reagents to the solution increases the precursor concentration above the nucleation threshold. Usually the crystal growth starts after the formation of a large number of nuclei by deposition of more products onto the nuclei. The size of the crystallites grows slowly and the reaction must be quenched at appropriate time to obtain nanocrystals of particular range of size. Sometimes arrested precipitation reactions can give colloidal suspensions of monodispersed particles. A synthetic route for CdS nanoparticles was put forward by Brus et al. which involves the controlled nucleation of CdS upon mixing of dilute aqueous solutions of CdSO₄ and (NH₄)₂S [68]. Most of the time, the reactions are so fast, that they can't be controlled easily. In some cases, better results can be obtained using a precipitation method, which is called precipitation from homogeneous solution.

Murray et.al developed a method for the preparation of semiconductor nanocrystallites by using tri-n-octylphosphine selenide (TOPSe) and hot tri-n-octylphosphine oxide (TOPO) [69]. This TOPO assisted method has the limitation of using hazardous compounds such as dimethylcadmium, [(CH₃)₂CdS] especially at high temperatures [70]. Molecular precursor method can overcome this by using single molecule precursors where a single compound (alkyldiseleno- or alkyldithiocarbamato complexes) containing all elements required for nanocystal synthesis [71]. Over the past decade, much progress has been made in the synthesis of quantum dots and nanoparticles using solution chemistry through hydrothermal or solvothermal route [72-74].
solvothermal method uses non-water solvents where the hydrothermal reactions use water as solvent. Moreover, the former method can effectively prevent the products from being oxidized during synthesis of non-oxides. The solvothermal reaction carried out in a sealed container results in increase in autogenous pressures and the reaction mixture can be brought to temperatures well above their boiling points.

Another method widely used is preparation of semiconductor nanoparticles in different matrices, such as zeolites [75], layered solids [76], molecular sieves [77], micelles/microemulsions[78,79], gels [80], polymers [81,82], and glasses [83,84] by melting and annealing processes, by organometallic chemistry or by sol-gel techniques. These matrices act as a boundary up to which crystallites can grow. More often, the range of particle sizes that can be prepared is limited to the pore size of the medium used as matrices.

Sol-gel processing (Figure 1.2) is a wet-chemical technique mainly for the production of glasses, ceramics, crystals, powders, thin films etc, through preparation of a sol, gelation of the sol and removal of the solvent. This route can be used to produce very sophisticated nanomaterials at relatively low temperature and consists of hydrolysis of the constituent molecular precursors and subsequent polycondensation. Semiconductor nanocrystals incorporated in glass matrices are potential materials and has been studied for nonlinear optical devices and phosphors [85-87].
Chapter 1

1.3 Nanosemiconductors

The first use of the term “nanotechnology” was by Norio Taniguchi in 1974 as “production technology to get extra high accuracy and ultra fine dimensions, i.e., the preciseness and fineness on the order of 1 nm (nanometer), $10^{-9}$ m in length” [88]. Later NASA gave the appropriate definition as “the creation of functional materials, devices and systems through control of matter on the nanometer length scale (1-100 nm), and exploitation of novel phenomena and properties (physical, p. 14).
chemical, biological) at that length scale” [89]. The large surface area/volume ratio exhibited by nanomaterials is the key advantage for their novel properties having potential applications. Another key factor for semiconductor nanoparticles is the size-tunable electronic properties due to quantum confinement effects.

Over the past decades, tremendous progress have been achieved in the field of nanotechnology with revolutionary changes in various applications ranging from biomedical sensing, solar energy conversion and energy storage to integrated optics. Being an active research domain, the semiconductor nanoparticles are curiously explored by scientists and engineers due to their superior transport and optical properties. In particular they have size tunable optical absorption thresholds and narrow and intense photoluminescence spectral features. Moreover, the chalcogen based semiconductors have been the focus for significant investigations for these applications.

1.3.1 Semiconductor nanoparticles doped silica matrix

It is possible to prepare highly photoluminescent glass by embedding water-soluble nanocrystals in a glass matrix using sol-gel process. As the nanoparticles are embedded in glass matrix, they are not subjected to surface oxidation. Sol-gel process includes a series of hydrolysis and condensation reactions in which the nanoparticles (colloidal sols) are formed from molecular precursors and aggregated to form a wet gel network. Depending upon how the wet gel is dried; the density and extent of porosity in the network can be effectively tuned. The sol-gel method has been widely exploited for the nanoparticle synthesis of many
oxides in the past, but there is a distinct advantage in moving to sulfide, selenide and telluride QDs because of the increased covalency (and decreased band gap) in the semiconducting phase. Semiconductor nanocrystals in transparent media especially in sol-gel glasses, have received recently a large attention due to their promising applications in non-linear optics and optical switches. For example, CdS, CdSe, CdTe and PbS exhibit a large optical non-linearity [90-92].

1.3.2 Polyvinylpyrrolidone modified quantum dots

Polymers are considered as good materials for preparing composites as they normally exhibit long-term stability and possess flexible reprocessability. Polyvinylpyrrolidone (PVP) was chosen as matrix for incorporating nanoparticles because of its unique characteristics. Since PVP is highly soluble in polar solvents such as alcohol, it is rather helpful to avoid phase separation in the reaction. PVP can be thermally cross linked [93,94] resulting in outstanding thermal stability and high mechanical strength of the hybrid material. Furthermore, the amorphous structure of PVP also provides low scattering losses and its transparent nature is a potential advantage for optical applications and device fabrication.

Nanostructured inorganic-polymer composites are receiving considerable interest for being novel composites with improved performance and outstanding properties. The PVP-capped CdSe nanoparticles embedded in PVA matrix were fabricated for photovoltaic applications [95]. The enhancement of the Sm\textsuperscript{3+} emission was observed in Sm\textsuperscript{3+}/TiO\textsubscript{2} nanocrystallites doped PVP matrix due to the energy transfer from TiO\textsubscript{2} nanocrystals to Sm\textsuperscript{3+} ions [96]. Moreover, surface
passivation of quantum dots (QDs) with PVP can enhance the luminescence properties as reported in ZnO QDs with strong ultraviolet emission [97].

![Structure of Polyvinylpyrrolidone Polymer](image)

**Figure 1.3 Structure of Polyvinylpyrrolidone Polymer**

### 1.3.3 Polyvinyl alcohol nanocomposite films

Polyvinyl alcohol (PVA) is a polymer of great interest due to its attractive properties with potential applications in papermaking, textiles, and a variety of coatings. Unlike many polymers, it is soluble in water and dissolves fairly fast into solution around 90°C. Polyvinyl alcohol is not built up in polymerization reactions from single-unit precursor molecules but is manufactured by the hydrolysis of polyvinyl acetate, in the presence of acids and alkalies. It is semicrystalline in nature with the following structure (Figure 1.4) It is composed mainly of 1,3-diol linkages [-CH\(_2\)-CH(OH)-CH\(_2\)-CH(OH)-] but a few percent of 1,2-diols [-CH\(_2\)-CH(OH)-CH(OH)-CH\(_2\)-] occur, depending on the conditions for the polymerization of the vinyl ester precursor. The major use of PVA as textile size give greater strength to textile yarns, particularly for
cotton-polyester blends. It can make paper more resistant to oils and greases. It is also employed as a thickening agent for various emulsion and component of adhesives.

![Structure of PVA polymer](image)

**Figure 1.4 Structure of PVA polymer**

For many of the optically active and laser materials like rare earths, dyes, metals and semiconductors [98-103], Poly Vinyl Acetate (PVA) is usually employed as matrix due to their high stability and optically transparent nature. Fabrication of PVA films with tunable and high dielectric constant has potential applications in charge storage devices [104]. One can tune the conductivity, dielectric and nonlinear optical properties of the PVA films by simply varying the concentration of the nanofillers introduced into the polymer matrix. Recently, second and third order optical nonlinear responses of PVA nanocomposite films doped with ZnSe nanocrystallites and PbS nanocrystallites were reported [105, 106]. Investigations on nonlinear optical behaviour of highly transparent ZnO/PVA nanocomposite films reveal that nonlinearity in the films arises from two photon absorption in ZnO [107]. Also ultrafast optical nonlinearity in free-standing Pt-polyvinyl alcohol nanocomposite films is reported to be controlled by varying the film composition and annealing temperature [108]. Long-time stable operation in mode-locking regime with high output power is achievable.
in an erbium doped fiber (EDF) laser where carbon nanotube dispersed in PVA matrix are used as passive mode-locker [109]

1.4 Free carriers and traps

Semiconductors which contain impurities or foreign atoms incorporated into the crystal structure are called doped semiconductors. These impurities can either be added purposefully to provide free carriers in the semiconductor. They can also be accidentally formed due to lack of control during the nucleation and growth of the nanocrystals. The free carriers are generated if these impurities give off electrons to the conduction band in which case they are called donors or that they provide holes to the valence band in which case they are called acceptors (since they effectively accept an electron from the filled valence band). Hence a doped semiconductor which is ionized (the impurity atoms either have donated or accepted an electron) will therefore contain free carriers.

The impurities can be termed as shallow and deep ones. Shallow impurities are those which need little energy (around thermal energy or less) to ionize. Thermal energy at room temperature is very small, i.e., 25 meV ($K T = 1.38 \times 10^{-23} J/K \times 300 K$). As deep impurities require energies larger than the thermal energy to ionize, only a fraction of the impurities incorporated in the semiconductor contribute to free carriers. Moreover, deep impurities held at more than five times the thermal energy away from either band edge are very unlikely to ionize. Such deep impurities can be effective recombination centers where electrons and holes fall and annihilate each other. They are also called traps. A semiconductor is
Chapter 1

called n-type, if impurities provide free electrons and if ionized acceptors provide free holes, it is referred to be a p-type semiconductor.

![Figure 1.5 Free carriers in p-type semiconductors](image)

1.5 **Defects in crystals**

Crystals may contain defects, as the arrangement of atoms is not perfect always due to the uncontrolled conditions under which they were formed. Depending on the dimensionality, crystal defects can be classified into four; point defects, line defects, planar defects, volume defects.

1.5.1 **Point defects**

The point imperfections are zero-dimensional defects such as vacancies, interstitials and impurity atoms purposefully added to the lattice or unintentionally incorporated into the crystal during growth process. The electronic defects such as holes and electrons also constitute to point defects. These are lattice errors at isolated lattice points.

1.5.2 **Line defects- edge dislocation and skew dislocations**

Line defects are dislocations within a crystal. A dislocation is the region where the arrangement of atoms is not perfect in the crystal.
General Introduction

lattice. An edge dislocation can be viewed as created when an extra portion of a plane of atoms is introduced in a crystal, the edge of the plane being in the crystal interior. Edge dislocation has their line segment perpendicular to the Burger vector. Dislocations whose line segments are parallel to the burger vector are skew dislocations. This can be viewed as formed by shearing the top part of the crystal with respect to the bottom part.

Figure 1.6 Point defects and Line defects

1.5.3 Planar defects - grain boundaries, stacking faults and twin boundaries

Planar defects occur whenever there is a discontinuity in the structure, such as interface of two surfaces, grain boundaries, etc.
boundaries, stacking faults and twin boundaries are planar defects (Figure 1.7). A grain is a portion of materials within which arrangement of atoms are nearly identical, however the orientation of atom arrangement or crystal lattice is different for each adjoining grains. The microstructure of nanomaterials consists of many grains. The surface that separates these adjoining grains is termed as grain boundary, a narrow zone where the atoms are not located properly. In some sites of grain boundary, the atoms are positioned very closely, creating a region of compression while in some locations; the atoms are loosely arranged that cause a region of tension.

Figure 1.7 Planar defects
An improper stacking sequence can produce two common types of crystal defects: 1) a stacking fault and 2) a twin region. An error in the stacking sequence over a few atomic spacing produces a stacking fault. For example, the normal stacking sequence of a perfect FCC lattice is ABCABCABC sequence. If instead the sequence produced is ABC ABAB CABC, the small portion indicated has a HCP stacking sequence instead of FCC sequence representing a stacking fault with one of the C planes missing. Similarly, if the hcp structure is going along as ABABAB and suddenly switches to ABABABCABAB, there is a stacking fault present.

A change in the stacking sequence over much atomic spacing produces a twin region. If a stacking fault does not correct itself immediately but continues over some number of atomic spacings, it will produce a second stacking fault that is the twin of the first one. For example if the stacking pattern is ABABABAB but switches to ABCABCABC for a period of time before switching back to ABABABAB, a pair of twin stacking faults is produced. The red region in the stacking sequence that goes ABCABCACBACBABCABC is the twin plane and the twin boundaries are the A planes on each end of the highlighted region.

1.6 Nonlinear optics

Physics would be dull and life most unfulfilling if all physical phenomena around us were linear. Fortunately, we are living in nonlinear world. While linearization beautifies physics, nonlinearity provides excitement in Physics — Y.R. Shen. Nonlinear effects in electricity and magnetism have been known since Maxwell’s time. In optical region, however, nonlinear optics became a subject of great common interest only after the laser was invented. In fact, the beginning...
of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken et al. in 1961, shortly after the demonstration of the first working laser by Maiman in 1960.

Nonlinear optics is the study of phenomena that occurs as a consequence of modification of optical properties of a material system by the presence of light. In general, the optical properties of a material do not depend on the intensity of the light incident on it. However, at high intensities, materials become optically nonlinear. The nonlinear absorption is considerably enhanced when the photon energy matches an optical transition in the material. Due to strong absorption and excitations across the band gap, semiconductor nanoparticles can have large nonlinear susceptibilities due to resonant optical nonlinearities. Nonlinear optical properties of semiconductor nanoparticles can be used to implement switches based on light energy, which are potentially much faster than electrical switches.

Nonlinear optics has a wide range of application in many areas such as communication and optical computing. Nonlinear optical materials include semiconductors, organics, liquid crystals, polymers, doped glasses, and porphyrins [110-115]. These materials can alter the properties of light propagating through them and hence can be used in a wide range of applications such as optical signal processing, optical switching, optical image processing, optical limiting of laser beams, laser beam shaping etc. Since hardly one material can possess all desirable characteristics, such as ultrafast response and a large value of optical
nonlinearity simultaneously, materials are chosen with their specific need for applications.

1.6.1 Light-matter interaction in the perturbative regime

When a neutral atom is placed in an electric field $E$, the nucleus is pushed in the direction of the field and the negatively charged electrons in the opposite direction. According to Lorentz model, when an alternating electric field is applied to an atom with one electron, the electron will start oscillating at the same frequency, which will radiate energy. At very low fields, however, equilibrium is soon established, leaving the atom ‘polarized’ with positive charge shifted slightly one way, and negative the other [116]. The induced polarization is directly proportional to the electric field as given by

$$P = \varepsilon_0 \chi^{(1)} E$$

(1.1)

where $\varepsilon_0$ is the vacuum dielectric constant, $\chi^{(1)}$ is the linear susceptibility, and $E$ is the amplitude of the electric field. $\chi^{(1)}$ is a second rank tensor since it relates two vectors $P$ and $E$ and is responsible for the linear optical properties like the refractive index($n_o$) and absorption coefficient($\alpha_o$) of the medium.

When the intensity of the incident light in a material system increases the response of the medium is no longer linear. Now the induced polarization is capable of multiplying the fundamental frequency to second, third order and even higher harmonics. It will depend on the higher powers of the electric field given by

$$P = \varepsilon_0 [\chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \ldots]$$

(1.2)

$$= P^{(1)(t)} + P^{(2)(t)} + P^{(3)(t)} + P^{(4)(t)} + \ldots$$

(1.3)
Chapter 1

The quantity $P^{(2)}(t)$ is known as second order nonlinear polarization and $P^{(3)}(t)$ as third order nonlinear polarization. Second order nonlinear optical interactions can occur only in noncentrosymmetric crystals; that is the crystals that do not display inversion symmetry. On the other hand, third order nonlinear optical interactions can occur for both centrosymmetric and non-centrosymmetric media. The optical nonlinearity is the property of the medium through which light pass through and not only the property of the light itself.

Depending on the initial and final quantum states of the system, nonlinear optical processes can be categorized as parametric and nonparametric. In parametric processes such as sum and difference frequency generation, second harmonic generation, optical parametric process etc. the initial and final quantum mechanical states of the system are identical.

1.6.2 Second order nonlinear effects

These effects are based on second order nonlinear polarization processes, and arise mainly from electronic cloud distortion mechanism. The nonlinear polarization then has a component, which depends quadratically on the electric field of an incident light wave. These nonlinear processes include second harmonic generation, optical sum and difference frequency generation and parametric amplification.

The process in which a monochromatic coherent optical wave can induce a new coherent wave emission at double frequency in a second-order nonlinear medium is called optical second-harmonic generation (SHG) or frequency doubling. Sum frequency generation is analogous to SHG, except that in sum frequency generation the two input waves are
of different frequencies. One of its applications is to produce a tunable radiation in UV region by choosing one of the input waves to be the output of a fixed-frequency visible laser and the other to be the output of a frequency tunable visible laser. In difference frequency generation, the frequency of generated wave is the difference of those of applied fields. Difference frequency generation can be used to produce tunable IR radiation by mixing the output of a frequency-tunable visible laser with that of a fixed frequency visible laser.

1.6.3 Third order nonlinear effects

Optical nonlinearity of the third order is a universal property, found in any material regardless of its spatial symmetry. This is the lowest order nonvanishing nonlinearity for a broad class of centrosymmetric materials where electric polarization can only have odd power electric field amplitudes. The third order polarization is given by

$$P(\omega_4) = e_0 \chi^{(3)} E(\omega_3) E(\omega_2) E(\omega_1)$$  \hspace{1cm} (1.4)

The essential feature of these effects is the nonlinear coupling between four coherent monochromatic optical waves; therefore they are also called four wave-mixing effects. In addition third order nonlinear polarization processes may also give rise to third harmonic generation, an induced refractive index change, two photon absorption etc.

1.6.4 Optical limiters: Application of nonlinear light transmission

The universal application of lasers brings about all dangers associated with high intensity of laser beam causing damage to optical sensors. Technologists and researchers are in search of new materials
with better efficiency to cut off the high intense laser beam while allowing passing less intense radiation. Such optical limiting materials transmit light till a threshold value at which it is clamped. The working of an ideal optical limiter is shown in Figure 1.8. If incident fluence is increased beyond $I_{th}$, the transmittance remains a constant. The lower the limiting threshold, more efficient the optical limiter is.

![Figure 1.8 Ideal optical limiting curve](image)

While considering optical limiting property, the process that attenuates laser beam intensity is nonlinear absorption and it is nonlinear absorption coefficient that determines whether or not a material can act as optical limiter. The change in transmittance of a medium as a function of the input light intensity or fluence is referred to as nonlinear light absorption or nonlinear light transmission.

### 1.7 Nonlinear absorption

The linear absorption coefficient of a medium depends on factors such as the transition probability and the concentration of the absorbing species. It will be independent of the input beam intensity, and only one
photon will be absorbed by an atom or molecule in a single event. However, at sufficiently high intensities, the probability of simultaneous absorption of more than one photon can be enhanced. Two-photon and multiphoton excitations are examples of such processes. In addition, intense laser fields can lead to population redistribution in complex molecules and the generation of free carriers in solids. Thus the transmittance of the medium will either be enhanced or reduced at high intensities. This change in transmittance of a material, which happens at high light intensity or fluence, is generally known as nonlinear absorption.

1.7.1 Saturable absorption (SA)

Saturable absorption is an example of non-parametric nonlinear process, the property of material whose transmission increases with laser light intensity. When sufficiently high intensity laser beam used, atoms or molecules in the ground state are excited into an upper energy state at such a rate that there is insufficient time for them to decay back to the ground state before the ground state becomes depleted. This leads to saturation of absorption in a saturable absorber material. Dependence of measured absorption coefficient on laser intensity is given by the expression,

$$\alpha(I) = \frac{\alpha_0}{1 + \left(\frac{I}{I_s}\right)}$$

where $\alpha_0$ is the low intensity absorption coefficient, and $I_s$ is saturation intensity. The main applications of saturable absorbers are in passive
mode locking and Q-switching of lasers, i.e., in the generation of short pulses [117].

1.7.2 Reverse saturable absorption (RSA)

Reverse saturable absorption (RSA) is a two-step, sequential one-photon absorption process usually occurs in systems such as polyatomic molecules and semiconductors. The samples giving RSA has a resonant linear absorption at the excitation wavelength, and some of the molecules in the ground state are excited to an excited state. After saturation of one photon, the molecules are further excited to higher state absorbing another photon of frequency $\omega$. Here the intermediate state is a real state and the excited-state cross section is larger than the ground-state cross section. If only a single excited state is taking part in the RSA process, the propagation equation can be written as,

$$\frac{dI}{dz} = -\sigma_0 N_0 I - \sigma_1 N_i I$$ (1.6)

where $\sigma_0$ and $\sigma_1$ are the absorption cross sections of the ground and the excited states respectively, $N_0$ and $N_i$ are the population densities of the ground and excited states respectively.

1.7.3 Two photon absorption (2PA)

In this process, system simultaneously absorbs two laser photons of frequency $\omega$ and makes transition from its ground state to an excited state approximately at resonant energy $2\omega$ (Figure 1.9). The intermediate level being virtual, the two photons should be simultaneously absorbed making the process sensitive to the instantaneous optical intensity of the incident radiation.
The propagation of the laser light (which is sufficiently intense to initiate the nonlinear light matter interaction), through the system describing the optical loss is given by

$$\frac{dI}{dz} = -\alpha I - \beta I^2$$  \hspace{1cm} (1.7)

where $\alpha$ is the linear absorption coefficient (which can be very small) and $\beta$ the two photon absorption coefficient.

The relation between the 2PA coefficient and the third order susceptibility of a centrosymmetric system for linearly polarized incident light is given as (in SI units):

$$\beta = \frac{3\pi}{\epsilon_0 n^2 c \lambda} \text{Im}[\chi^{(3)}_{\omega\omega\omega\omega} (-\omega; \omega, \omega, -\omega)]$$  \hspace{1cm} (1.8)

It is the imaginary part of the third order nonlinear susceptibility of the system that determines the strength of the two photon absorption.

![Figure 1.9 Schematic diagram of two photon absorption](image)

To quantify nonlinear absorption, transmittance can be conveniently measured as the ratio of the transmitted and incident energies. For a pulsed laser beam that is spatially and temporally Gaussian, the
transmittance $T$ in the presence of two photon absorption is given by [118]

$$T = \left[(1 - R)^2 \exp(-\alpha L) / \sqrt{\pi q_0} \right]^\infty_{-\infty} \ln\left[1 + q_0 \exp(-t^2)\right] dt$$

(1.9)

where $L$ and $R$ are the sample length and surface reflectivity, respectively, and $\alpha$ is the linear absorption coefficient. $q_0$ is given by 

$$q_0 = \beta(1 - R) I_0 L_{\text{eff}}$$

where $\beta$ is the two photon absorption coefficient, and $I_0$ is the peak on-axis intensity incident on the material. Also $L_{\text{eff}}$ is given by

$$L_{\text{eff}} = \frac{\alpha}{\alpha L} I_0$$

### 1.7.4 Three photon absorption (3PA)

The process of the transition of a system from the ground state involving simultaneous absorption of three laser photons of frequency $\omega$ to an excited state approximately at resonant energy $3\omega$ is termed as three photon absorption (Figure 1.10). This process involves two virtual states as intermediate energy levels. 3PA is a fifth-order nonlinear process, and the propagation equation for a medium having significant three photon absorption is given as,

$$\frac{dl}{dz} = -\alpha l - \gamma I^3$$

(1.10)

where $\gamma$ is the three-photon absorption coefficient which is related to the imaginary part of the fifth-order susceptibility through

$$\gamma = \frac{5\pi}{\varepsilon_0 n^2 c^3 \lambda} \text{Im}[\chi^{(5)}_{\text{xxxx}} (-\omega; \omega, \omega, -\omega - \omega)]$$

(1.11)
When a spatially and temporally Gaussian laser beam incident on a system having three photon absorption property, the transmittance is given by [118],

\[
T = \left( \frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{2\pi p_0}} \right) \int_{-\infty}^{\infty} \ln \left[ \sqrt{1 + p_0^2 \exp(-2t^2)} + p_0 \exp(-t^2) \right] dt
\]

where, \( p_0 \) is given by \( \sqrt{2\gamma(1-R)^2 I_0 L_{\text{eff}}} \) where \( \gamma \) is the three-photon absorption coefficient, and \( I_0 \) is the peak on-axis intensity incident on the material. Also \( L_{\text{eff}} \) is the effective length in the medium given by \( \frac{[1 - \exp(-2\alpha L)]}{2\alpha} \).

### 1.7.5 Excited state absorption (ESA)

In this process, the system absorbs one photon of frequency \( \omega \) and gets excited by the incident laser light. The excited system further absorbs another photon of the same frequency and makes transition to
higher state (Figure 1.11). This process looks similar to two photon absorption but here the intermediate level is a real state.

![Figure 1.11 Schematic diagram of excited state absorption](image)

**1.7.6 Free carrier absorption**

In semiconductors due to linear absorption, free carriers (electrons in the conduction band and holes in the valence band) are generated. At sufficiently high intensities they may experience excited-state absorption to higher-lying (lower-lying) states in the conduction (valence) band known as free carrier absorption.

In the weak absorption regime, the attenuation may be described by

$$\frac{dl}{dz} = -\alpha l - \sigma_c N_c l^2$$

(1.13)

where $\sigma_c$ is the intensity dependent carrier density and $N_c$ is the free carrier absorption cross-section. Free carrier absorption is a major
underlying factor for optical limiting in semiconductors, semiconductor quantum dots and metal nanoparticles.

1.8 Generation of ultrafast laser pulses

1.8.1 Femtosecond laser system

To examine ultrafast optical nonlinearity, we used ultrafast laser pulse from Ti:Sapphire femtosecond laser system for our experiments (Tsunami and TSA-10, Spectra Physics). Femtosecond pulses are generated from the spectra physics Ti:sapphire oscillator (Tsunami, Spectra Physics) with a one centimeter long Ti:sapphire crystal rod as lasing material. The Ti$^{3+}$ titanium ion is responsible for the laser action of Ti:sapphire. A frequency doubled CW diode pumped Nd:YVO4 laser (Millennia Pro, Spectra Physics) at 532 nm with an output power of up to 5.2 W is used to pump Ti:sapphire crystal. A diode laser (809 nm, 40 W) act as pump for Nd:vanadate crystal which is coupled via an optical fiber module. Using a Lithium Triobate (LBO) crystal, the fundamental emission from vanadate crystal is frequency doubled to generate an output of 532 nm.

The Ti:sapphire oscillator consists of a folded cavity with an acousto-optic modulator (AOM) and active feedback for generation of ultrashort pulses by regenerative mode-locking technique. The optics that form the resonator cavity includes pump beam mirrors, rod focusing mirrors, an output coupler (OC), a high reflector (HR), beam folding mirrors, dispersion control elements, and tuning elements. Dispersion control of the laser cavity is achieved with a pair of prisms, and an adjustable slit is used for wavelength selection. The ultrafast oscillator produces
Chapter 1

Gaussian pulses of approximately 100 fs duration at a repetition rate of 82 MHz of about 1 nJ energy per pulse. The output wavelength can be tuned from 700 nm to 1000 nm (Tsunami broadband version). A maximum average power output of 550 mW can be obtained at 809 nm, which is the peak of the tuning curve.

Figure 1.12 Schematic of the ultrafast CPA laser used for the z-scan experiment.

High energy ultrafast pulses are obtained using a technique called chirped pulse amplification (CPA). In titanium sapphire amplifier (TSA 10, Spectra Physics) the pulses are stretched to about 300 ps to reduce the peak power. An individual pulse is then picked using an electro-optic modulator and is amplified in a regenerative cavity with Ti:sapphire
crystals as the gain medium. The pulse oscillates in the cavity to achieve sufficient energy. It is then reflected out of the cavity using an electro-optic switch and is fed to a double-pass cavity for further amplification. After amplification, the original input pulse width can be obtained back by compressing the pulse by using a grating compressor. The TSA-10 generates 100 fs pulses of 10 mJ energy at a repetition rate of 10 Hz. The pump laser for CPA is a frequency doubled, Q-switched Nd:YAG laser (Quanta Ray, Spectra Physics) operating at 10 Hz with a nominal pulse width of 7 ns. It is capable of generating pulses with 275 mJ energy at 532 nm, where the frequency doubling is done using a KDP crystal. Schematic of the ultrafast CPA laser used for the z-scan experiment is shown in Figure 1.12.

1.9 Z-scan technique

As the phenomenon of nonlinear transmission depends on the intensity of laser light, we need a path of varying intensity to examine the nonlinear absorption in materials. Such a path can be obtained by focusing the laser beam using a lens. This simple idea is the essence of z-scan experiment, which has become quite popular for nonlinear absorption measurements [119]. The direction of the focused beam propagation is taken as the z-axis, and the focal point is considered as z = 0. This method compared with others, e.g., four wave mixing phase conjugation and interferometric method, exhibits high accuracy, sensitivity, and ability to determine the sign of the optical nonlinearities. Analysis of the transmittance versus sample position represents the z-scan curve which gives the real and imaginary part of third order nonlinear susceptibility. The real part and imaginary part of
third order nonlinear susceptibility is related to non-linear refraction and nonlinear absorption, which is determined from closed aperture z-scan and open aperture z-scan respectively. A schematic of the z-scan setup can be seen in Figure 1.13

![Figure 1.13. Schematic of the closed aperture and open aperture z-scan setup.](image)

### 1.9.1 Closed aperture z-scan technique

In this technique, the transmittance of a tightly focused Gaussian beam through a finite aperture in the far field is measured as a function of the sample position $z$ with respect to the focal plane. Consider a laser beam with a Gaussian beam cross-section, given by

$$I_0 = \exp\left(\frac{-2r^2}{\omega^2}\right)$$

where $\omega$ is the beam radius and $r$ is the radial co-ordinate. The intensity will be maximum at the beam center, which will drop exponentially along the radial direction. Therefore when a Gaussian
laser beam passes through a nonlinear medium, it will see maximum refractive index at the beam center, which will gradually decrease along the radius direction. This result in phase modulation of the wavefront. As a result, the beam will get focused by itself if $n_2$ is positive, and if $n_2$ is negative, then the beam will be defocused. Such defocusing/defocusing is usually small, sufficient intensity ($I$) is required to get a measurable effect.

### 1.9.2 Experimental technique for nonlinear absorption measurements

In open aperture z-scan the sample is translated along the axis of the focused Gaussian beam, in and out of the focal region of an incident laser beam thereby varying the intensity of light falling on the sample. The far field intensity is measured as a function of sample position. In open aperture z-scan technique, the detector will measure all the light transmitted by the sample, as no aperture is kept between sample and detector. As the sample moves through the focused beam, there occurs increase or decrease in transmittance with intensity, as there is maximum intensity at the focus of the lens. For RSA it will be a minimum, and for saturable absorption it will be a maximum at the focus. The required scan range depends on the beam parameters and the sample thickness $d$. A critical parameter is the Rayleigh range, $z_0$ of the Gaussian beam with waist $\omega_0$, of focused beam defined as $\frac{\pi \omega_0^2}{\lambda}$. It is preferable to scan sample of thickness less than $\approx \pm 5z_0$. 
1.9.3 Evolution of optical Nonlinearity - ns to fs excitation domains

The optical limiting property is wavelength tunable as well as pulse-width dependent. The genuine 2PA coefficient is pulse duration independent whereas effective 2PA coefficient measured depends on the laser pulse width [120]. For excitation at ns and fs time domains, the effective contributions are different.

![Schematic illustration of excitations and relaxations in ns and fs excitation regimes](image)

**Figure 1.14** Schematic illustration of excitations and relaxations in ns and fs excitation regimes

For long pulse width excitations, after one photon or two photon excitations, other excitations and relaxations are possible within the pulse duration. The molecule excited to the higher states through one photon or two photon can relax down within a short time scale (ps or fs). This can further absorb another photon from the same pulse and get excited with long pulse excitations (ns). Similarly, molecule in an excited state with a longer life time can get further excited to higher levels by...
absorbing photons from the same pulse before returning to ground state. This cumulative effect adds to the 2PA coefficient resulting in a higher value of effective two photon coefficient. At the same time, with fs pulses, the excited molecule can still absorb one photon, but before it gets relaxed, the pulse might have passed the material (Figure 1.14). Thus ESA obtained for ns pulses will be usually larger than the value obtained from ultrafast excitations.

1.10 Organization of the thesis

The present thesis is a study on synthesis of certain chalcogen based nanomaterials and their interaction with moderately intense nanosecond and femtosecond laser pulses. A review of chalcogen based nanomaterials, a general introduction on synthesis and nonlinear optics is given in this chapter. Chapter 2 elaborates ultrafast (fs) and short (ns) laser pulse induced optical nonlinearity in nanostructured Se allotropes. In chapter 3, a novel sol gel method to obtain two different forms of selenium; namely, cubic and amorphous Se nanoparticles doped silica is discussed. Investigations on their optical and ultrafast nonlinear optical properties are also included. Chapter 4 describes systematic investigation of the preparation of CuS quantum dots and nanoparticles, their microstructural defects, crystalline, optical and nonlinear optical properties. Chapter 5 depicts a simple, facile route developed for preparing silica hybridized CuS, Ag₂S CuS-Ag₂S nanocomposites and their alloy at room temperature and their crystalline, structural, optical and optical limiting (OL) properties. Chapter 6 is a study of structural, optical dielectric and ultrafast nonlinear optical properties of poly-vinyl
acetate films doped with CuS, Ag₂S, CuS-Ag₂S nanocomposite and alloy nanoparticles. Chapter 7 contains the conclusions drawn from the studies and some future perspectives.

1.11 Aims and objectives of the work

1.11.1 Aims

The aim of the work presented in the thesis is twofold. First was to prepare certain chalcogen based nanomaterials having relevant nonlinear optical applications. Second part was focused to investigate nonlinear optical absorption in these nanomaterials which is useful for designing good quality optical limiters.

1.11.2 Objectives of the work

- To develop a novel, simple, non-toxic and green synthetic route to prepare high quality, monodispersed, amorphous and trigonal, selenium nanoparticles and nanowires respectively without complicated equipment or organometallic precursors.
- To obtain cubic form of selenium, an unexplored allotrope through sol gel route in addition to amorphous selenium nanoparticles incorporated in the silica matrix.
- To synthesize water-dispersible CuS quantum dots and nanoparticles capped with polyvinylpyrrolidone through a one-pot synthesis using water as the solvent.
- To prepare silica hybridized CuS, Ag₂S, Ag₂S-CuS nanocomposites at room temperature.
To develop poly-vinyl acetate (PVA) free standing films doped with CuS, Ag₂S, CuS-Ag₂S nanocomposite and alloy nanoparticles.

To investigate morphology, crystalline and optical properties of the prepared chalcogen based nanomaterials and to study the improved dielectric constant of nanofillers doped PVA films.

To explore the nonlinear optical properties and to determine various nonlinear transmission phenomena taking place in the system using z-scan technique.
Chapter 1

References

Chapter 1

General Introduction


Chapter 1


