Chapter 1

CHAPTER 1

INTRODUCTION
1.1 Introduction

Among the wide variety of sciences, Material Science is an important part which deals with the relationship between structure and properties of the materials. It includes examining how the structure, whether crystalline or amorphous, can be changed to affect the properties of the material. Materials are divided into different categories on the basis of different parameters viz; (i) the chemical composition of the material (ii) the mode of occurrence of the material in nature (iii) the refining and the manufacturing process to which the material is subjected prior to acquiring the required properties (iv) structure of material and (v) the industrial and technical use of the material.

Solid, liquid, gas and plasma are the common states of matter which are classified on the basis of particle arrangement, energy of the particles and distance between the particles. Solids are the particular state of condensed matter characterized by strong bonding between the constituent particles (atoms, molecules). Generally, solids are characterized into two forms; crystalline solids and non-crystalline solids (amorphous solids). In crystalline solids the building constituents arrange themselves in regular manner throughout the entire three dimensional networks. In a monocrystalline material, the periodicity extends throughout the material and there are no grain boundaries. Due to the absence of the defects, correlated with grain boundaries, the monocrystalline material has unique electrical, optical and mechanical properties which are useful in optics and electronics. Many tiny crystals of different size and orientations come together to form a polycrystalline material in which periodicity is disturbed at the grain boundaries.

When the size of the grains become comparable to the size of the pattern unit, then one can talk about non-crystalline, amorphous or vitreous solids. The amorphous state is the disordered state of the solid i.e. arrangement of atoms is not well defined. Absence of long range order compared to crystalline solids is the main specialty of the structure of the amorphous state. The periodicity in the amorphous solids lies in range of 10-15 Å. Each unit cell in the amorphous solids differs from the proceeding one in its position in space.

1.2 Structure of amorphous materials

The detailed analysis of physical and optical properties of the solids requires an idea about the structural arrangement of atoms in crystalline or amorphous solids. The
arrangement of atoms in crystalline and amorphous solids is shown in Figure 1.1. In Figure 1.1 the solid spheres denote the equilibrium position about which the atoms oscillate.

![Figure 1.1](image)

Figure 1.1 Comparison of the atomic arrangements in (a) a perfect crystal and (b) an amorphous semiconductor. The atomic structure shown here is three-fold coordinated, with the atoms labeled with U are under- and atoms labelled with O are over-coordinated.

As translational periodicity exists in crystalline structure, consequently almost all the bond angles and bond lengths are same. Therefore in crystalline solids, long range order exists all over the solid. But in amorphous solid there are small variations in bond angles and bond lengths. Due to these variations, the periodicity in amorphous solids exists not more than few atomic radii. Topological disorder arises in amorphous solids due to short range order. Due to this type of disorder, in certain amorphous solids the bonding requirement is unsatisfied and formation of dangling or broken bonds takes place. Spin disorder, compositional disorder and vibrational disorder are the other types of disorder in amorphous solids. In amorphous solids, there is a high degree of short range order as compared to crystalline solid. In amorphous solids, the valence requirement is satisfied for each atoms and each atom is bonded with the same number of nearest neighbors. Hence it
can be stated that no solid is exactly “amorphous” in the sense of totally missing in any type of definable order [1, 2].

1.3 Band models for amorphous semiconductors

To understand the electronic properties of the materials the knowledge of their electronic band structure is very important. In crystalline semiconductor, the sharp edges in density of states produce well-defined forbidden energy gap. This is due to perfect short range order and long range order in crystalline solids. The short range order of amorphous solids appears as that of crystalline one which indicates that density of states is also applicable for amorphous solids. The electrical and optical properties of amorphous solids in terms of ‘states in gap’ have been explained by using different models. It was Mott [3, 4] who first generalized the concepts of crystalline semiconductor to amorphous ones on the basis of Anderson’s theory [5]. According to Mott, the localized states are formed in amorphous materials which do not occupy all the energy states in the band, but form a tail above and below the normal band because of the configurational disorder in the system. At mobility edges, the localized states are separated from the extended states [6]. In a semiconductor the electronic states consists of delocalized states like conduction band and valence band, also called extended states. Localized states are constituted by tails and dangling bonds. The extended states are due to short range order whereas tail states are due to translational and compositional disorder. Tail states are supposed to cause fluctuations of the potential of sufficient magnitude such that it gives rise to localized states extended from the conduction and valence bands in the forbidden energy gap. Several models have been proposed for understanding the feature of amorphous semiconductor. Three models are given below to describe the structure of amorphous materials.

1.3.1 CFO Model/ Mott-CFO Model

CFO model [7] is an extension of Mott’s model. According to this model, the tail states in a structure less distribution extend across the gap. The sharpness of the conduction and valence band edges destroys due to gradual decrease of the localized states. The wide tailing of the localized states makes the conduction band and valence band tails overlap in the mid gap, leading to an appreciable density of states in the middle of the gap. Due to this overlapping, there are filled states in valence band with higher energy as compared to empty states in conduction band. After the redistribution of electrons, filled states are
formed in conduction band which are negatively charged and empty states in valence band which are positively charged. This model is best for multi-component chalcogenide glasses used in switching devices.

![Sketch of the partial densities of states of the valence and conduction bands.](image)

**Figure 1.2** Sketch of the partial densities of states of the valence and conduction bands.

### 1.3.2 Davis-Mott model

This model was suggested by Davis and Mott [8] in the Figure 1.3. $E_c$ and $E_v$ are the mobility edges for electron and holes respectively. There is a difference between localized states that are generated from the lack of long range order and others which are due to defects in the structure. The longer tails that are generated by defects have insufficient density to pin in the Fermi level, but the authors [8] have suggested a band of compensated levels near the gap center in order to pin the Fermi level.

### 1.3.3 Marshall-Owen model

It was Marshall and Owen in 1971 to propose a model first for showing gap and therefore called the Marshall-Owen model [9]. According to this model, the position of the Fermi level is determined by bands of donors and acceptors in the upper and lower halves of the mobility gap, respectively. The level of donors and acceptors adjust themselves by
self-compensation to be nearly equal so that the Fermi level occurs at the center of the gap. Because at low temperature, self-compensation is not likely to be complete so that Fermi levels moves to one of the impurity bands.

Figure 1.3 Sketch of Mott and Davis Model.

Figure 1.4 Sketch of Marshall-Owen model.
1.4 Defect Models

The electronic and transport properties of the materials are determined using defects. Different models have been proposed for defining the defects in amorphous materials which are discussed below.

1.4.1 Mott, Davis and Street

Mott, Davis and Street [10-11] have suggested a model for the defect states in the gap of amorphous semiconductors. According to Mott [12] the dangling bonds are originated by the bands of localized states. Chalcogenide glasses contain $10^{18} - 10^{19}$ cm$^{-3}$ dangling bonds. There are three dangling bond states; $D^+$, containing zero electrons, $D^0$ containing one electron and $D^-$, containing two electrons. The lattice distortion and energy level is used to define the dangling bond energy level. The major objection to this model is the assumption of high density of dangling bonds. Also the model doesn't explain large negative effective correlation energy for chalcogenide glasses and why it is absent in tetrahedral bonded amorphous materials [13].

1.4.2 KAF Model

This model is recommended by the Kastner, Adler and Fritzschke [14] for the formation of valence alteration pair (VAP). The energy of formation for VAP’s is so small that their density in most of the glasses is relatively high. They suggested that in the ground state each chalcogen atom will form one positively charged three fold coordinated atom, and one negatively charged, one fold coordinated atom, i.e., $2C_3^0 \rightarrow C_3^+ + C_1^-$. VAP formation cannot occur in group IV atoms because they cannot be fivefold coordinated but it takes place in group V atoms.

1.5 Glasses

It was Faraday (1830) who first studied the nature of glasses in a basic manner. In the 19th century he started working with optical properties of glasses. In the 1950’s and 1960’s it was discovered that glass could be formed by many materials like polymers, salt, chalcogenide and even metals. The easy manufacturing of glasses as compared to crystalline materials motivated researchers to analyze their various properties.

To avoid the crystallization, the liquid is cooled fast enough and solidified to a metastable disordered state. This metastable state is called amorphous state. A discontinuous decrease in the volume of the system in liquid – crystal transition takes place
with slow cooling rate. But there is a continuous decrease in volume when temperature passes through a threshold value called glass transition temperature with fast quenching. The disordered solid that consist of glass transition temperature is called glass. Glasses are further classified into two groups tetrahedral coordinated glasses and chalcogenide glasses.

1.5.1 Tetrahedral glasses

Tetrahedral glasses are formed by the fourth group amorphous semiconductors silicon (Si) and germanium (Ge). Thermal evaporation or sputtering technique is used for the formation of amorphous Si and Ge in pure form. In amorphous Si and Ge, the atoms have four bonds and the average bond angle is 109.5°. Similar is the case with hydrogenated Si (a-Si:H) in which hydrogen forms one bond. The a-Si: H and its alloys have great applications in wide area of electronic devices like solar cells and displays.

1.5.2 Chalcogenide glasses

The elements Sulphur (S), Selenium (Se) and Tellurium (Te) belonging to group VI of periodic table are known as chalcogens. Chalcogenide glasses are formed by the combination of these chalcogens with electropositive materials and radicals. The four fold coordination in Si leads to the generation of more symmetrical and rigid structures. On the other hand, two fold coordination in chalcogen leads to the formation of asymmetrical and flexible structures. Accordingly, the chalcogenide structure is more complicated than that of tetrahedral bonded glasses like Si and Ge. Chalcogenide glasses have chain or ring type structures leading to the absence of long range order. In general, chalcogenides are good glass formers and can be prepared by both cooling from liquid and vapor deposition. The most studied chalcogenide systems are a-Se, As₂Se₃, GeSe₂.

As chalcogenides have lone pair electrons and show semiconducting properties, accordingly chalcogenides are also named as lone–pair semiconductors. The occurrence of lone pairs enhances the flexibility of the bond-angles which further decrease the strain energy in the system. This causes the atoms to easily generate the amorphous structure. These structures may occur in elemental form like S, Se, binary form As₂S₃, As₂Se₃ or in multicomponent forms like Ga₅Sb₅Ge₂₅Se₆₅, Sr₃Ge,Sb₂Se₈. The ring or chain type structures in elemental or binary chalcogenides extend in one or two dimensions. The limit of short order is vast in elemental or binary glasses. In contrast, multicomponent glasses have three dimension structures and accordingly, have smaller limit of short order.
1.6 Review of Literature

1.6.1 History of chalcogenide glasses

It is difficult to mention a date when the chalcogenide glasses were used in the field of technology. In early years, vitreous glassy state has been used in the form of oxygen and its compounds. It was Schulz- Sellack [15] who first reported data on oxygen free glasses in 1870. At the end of 19th century vitreous selenium and arsenic selenide and sulphides were synthesized first time. In the 20th century vitreous selenium became the promising material in the field when Wood [16] reported the optical properties of these materials. In the 20th century growth in the field of IR optics led to the requirement of new IR materials. The transparency of oxide glasses in the IR region is from 3µm to 8 µm, whereas for chalcogenides it extends upto 20 µm.

It was Freriches who worked on chalcogenide glasses first in early 1950’s on the composition As$_2$S$_3$ [17,18]. Chalcogenide glasses were discovered as a semiconducting material by Goriunova and B.T. Kolomeits. The first method for the preparation of glasses at industrial scale is discovered by Glaze and co-workers [19]. In 1960’s it was Loffe [20] who first pointed out that electronic properties of a solid depends on the existence of short range order rather than on the long range order of the lattice. The switching property in chalcogenide glasses is discovered by Ovshinsky in 1968 [21] and this led to the usage of chalcogenide glasses in various fields like memory devices and xerography. The theory on electronic process in chalcogenide glasses is discovered by N. F. Mott and E. A. Davis [4].


1.6.2 Linear optical properties

Optical properties describe the interaction between light and matter, when light passes through it. It leads to many optical phenomena. The interaction of light with material is explained in terms of dielectric response of the material. The complex refractive index determines the dielectric response. The optical properties viz; refractive index (n), extinction coefficient (k), absorption coefficient (α) and optical band gap (Eg) of various chalcogenide glasses have been reported by many researchers [29-51].

The optical properties of AsxSe100-x (x = 50, 57.1, 60) amorphous thin films have been studied by Nemec et al. [29]. Thin films were deposited by pulsed laser deposition technique (PLD) and thermal evaporation technique (TE). The values of Eg are found to decrease for PLD films and increase for TE films with the increase of As content. Shaaban et al. have studied the optical properties of amorphous As40S60, As35S65 and As30S70 thin films [30]. The value of n increases while the value of Eg decreases with the increase of As content. Shaaban et al. [31] used transmission spectra in the spectral range 400-2500 nm for the analysis of optical properties of amorphous Se70S30 thin films. The value of n decreases with increasing wavelength and reported value of Eg is 2.25 eV.

The optical properties of amorphous Se80Te20 thin films have been studied by Mainka et al. [32]. The reported value of n is 3.37 and the value of Eg is 1.41 eV.

Aly has studied the optical properties of amorphous Se70Te30 and Se70As30 thin films [33]. The reported value of n for Se70Te30 thin films is larger and value of Eg is smaller than Se70As30 thin films.

The effect of laser irradiation on the optical properties of thermally evaporated Se100-xTex (x = 8, 12, 16) thin films have been studied by Bahishthi et al. [34]. The results indicate that there is a shift in the Eg due to laser irradiation. The result shows that the value of
absorption coefficient ($\alpha$) increases and $E_g$ decreases with the incorporation of Te content and with laser irradiation.

Mishra et al. utilized transmission spectra in the spectral range 300-1200 nm for the analysis of optical properties of Se$_{80}$Te$_{20}$ thin films [35]. The reported value of $n$ and $E_g$ are 1.76 and 0.55 eV, respectively.

The optical properties of amorphous Se$_{90}$In$_{10-x}$Sn$_x$ ($x = 2, 4, 6, 8$) thin films of thickness 1000 Å have been studied by Shaheen et al. [36]. The result shows that the value of $E_g$ decreases with the incorporation of Sn content.

Pan et al. have carried out work on the optical study of amorphous (GeSe$_2$)$_{100-x}$Bi$_x$ thin films deposited by the pulsed laser deposition technique [37]. With Bi addition to the base composition transmission spectrum shift towards the longer wavelength. The result shows that with Bi addition, the value of $n$ increases while $E_g$ decreases.

Sharma et al. have reported the optical study of Ge$_{10}$Se$_{90-x}$Te$_x$ glassy semiconductors [38]. A red shift has been observed in the transmission spectrum with the addition of Te content to the base composition. Firstly, the value of $n$ decreases (upto 30 atomic %) and thereafter increases with the increase of Te content.

Petkova et al. [39] have done the optical study of (AsSe)$_{100-x}$Sb$_x$ thin films. The optical parameters have been calculated with the help of transmission and reflection spectra in the spectral range of 400-2500 nm. The result shows that the value of $n$ increases while $E_g$ decreases.

Saleh et al. [40] have reported the optical study of ternary Sb$_{65}$Se$_{35-x}$Ge$_x$ ($x = 0$-20 atomic %) thin films prepared by electron beam evaporation technique. With the incorporation of Ge content to the base composition $E_g$ decreases.

Shaaban et al. [41] utilized transmission spectra for the analysis of optical study of Sb$_x$Ge$_{25-x}$Se$_{75}$ ($x = 0, 5, 10, 15, 20$) thin films. It has been observed that $E_g$ decreases with the incorporation of Sb content. Othman et al. [42] have done the optical study of As$_{30}$Sb$_{15}$Se$_{35}$ composition. The reported value of $E_g$ is 1.49 eV.

Wang et al. have reported the optical study of Se$_x$Ge$_{25-x}$Te$_{75}$ ($x = 0, 5, 10, 15, 20$) glasses [43]. Blue shift has been observed in the transmission spectra and hence $E_g$ increases with the increase of Se content.
Sharma et al. have studied the optical properties of amorphous \((\text{As}_2\text{Se}_3)_90\text{Ge}_{10}\)\(_{95}\)Cd\(_5\) and \((\text{As}_2\text{Se}_3)_90\text{Ge}_{10}\)\(_{95}\)Pb\(_5\) thin films [44]. The reported value of \(E_g\) for \((\text{As}_2\text{Se}_3)_90\text{Ge}_{10}\)\(_{95}\)Cd\(_5\) is 1.36 eV and 2.86 eV for \((\text{As}_2\text{Se}_3)_90\text{Ge}_{10}\)\(_{95}\)Pb\(_5\) thin film.

The effect of In on the optical properties of \(\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25}\)\(_y\) \((y = 0, 3, 6, 9, 12, 15)\) chalcogenide thin films have been studied by Sunanda et al. [45]. With the incorporation of In content, a red shift has been obtained in the transmission spectra. With the addition of In content, value of \(n\) increases while value of \(E_g\) decreases.

Pankaj et al. have studied the effect of Sn on the optical properties of As–Se–Ge films deposited by thermal evaporation technique [46]. The result shows that with the incorporation of Sn to the system, value of \(n\) increases from 2.64 to 2.95 while the value of \(E_g\) decreases from 1.46 eV to 1.37 eV.

Sharma et al. [47] have studied the optical constants of quaternary chalcogenide \(\text{Ge}_{20}\text{Se}_{70-x}\text{In}_x\text{Bi}_x\) \((x = 2, 4, 6, 8, 10)\) thin films. With the addition of Bi content, absorption edge has been found to shift towards longer wavelength. The result shows that with the addition of Bi content to the system, values of \(n\) and \(K\) increases while the value of \(E_g\) decreases.

Dahshan et al. have utilized transmission spectra for the optical study of \(\text{As}_{14}\text{Ge}_{14}\text{Se}_{72-x}\text{Sb}_x\) \((x = 3, 6, 9, 12)\) thin films. With the replacement of Se by Sb, value of \(E_g\) decrease from 1.72 to 1.56 eV.

Pankaj et al. have done the optical study of quaternary chalcogenide \(\text{Ge}_{20}\text{Se}_{60}\text{Sb}_{20-x}\text{Ag}_x\) \((x = 0, 5, 10, 15, 20)\) thin films [49]. Blue shift has been observed in the transmission spectra with the incorporation of Ag content to the base composition \(\text{Ge}_{20}\text{Se}_{60}\text{Sb}_{20}\). Hence \(E_g\) increases (1.37 to 1.55 eV) with increase of Ag content while the value of \(n\) decreases.

Aly [50] has utilized reflection spectra for the optical study of amorphous Ge-As-Te-In thin films. The result shows that \(E_g\) decreases with the addition of In content.

The optical transmission spectra of \(\text{Sn}_{10}\text{Sb}_{20-x}\text{Bi}_x\text{Se}_{70}\) \((0.6 \leq x \leq 6.8)\) thin films in the range of 400-2500 nm have been studied by Ahmad et al. [51]. With an increase in wavelength, the values of \(n\) and \(a\) decreases. The value of \(E_g\) first increases with Bi content (for \(x = 2\) atomic percent) and then decreases for higher concentrations of Bi.

1.6.3 Nonlinear optical properties

Due to wide applications in optical communication and data storage technology,
optics became well-known among researchers. The area of nonlinear optics deals with the interaction of high intensity field with matter. “Nonlinear” means that the response of material to an applied field depends nonlinearly on the strength of the optical field. The optical properties of material like refractive index ($n$), absorption coefficient ($\alpha$) have been observed to modify in the presence of laser light. The nonlinear optical properties like nonlinear refractive index ($n_2$), two photon absorption coefficient ($\beta_2$) and third order susceptibility ($\chi^{(3)}$) of various chalcogenide glasses have been studied by many authors theoretically and experimentally [52-63].

The optical nonlinearity of binary chalcogenide As$_2$S$_3$ thin film as well as in bulk form has been studied by Sunita et al. [52] using Z-scan technique. The result shows that the nonlinear optical parameters of thin films are higher than bulk glasses.

The enhanced nonlinear optical properties of As$_2$Se$_3$ chalcogenide thin films have been studied by Se-Young Kim et al. [53]. The reported value of two photon absorption coefficient is $1.59 \times 10^{-8}$ m$^2$/W and value of nonlinear refractive index is $1.268 \times 10^{-5}$ m$^2$/W. Author’s have reported that these materials are advantageous for super-RENS, which improves the density and the response time of optical recording disk.

The optical nonlinearity in binary Ge-Se and ternary Ge-Se-As chalcogenide glasses has been reported by F. Smektala et al. [54]. The reported value of $n_2$ for binary Ge-Se and ternary Ge-Se-As chalcogenide glasses is $8.0 \times 10^{-18}$ m$^2$/W and $10.2 \times 10^{-18}$ m$^2$/W respectively. Author stated that the high value of $n_2$ make these glasses beneficial for ultrafast all-optical applications.

R. tintu et al. [55] has done the nonlinear optical study of nano colloidal Ge$_{28}$Sb$_{12}$Se$_{60}$ chalcogenide glass. The nonlinear optical study revealed that these glasses are predominate material for optical limiting devices due to high transmission at 532 nm, strong nonlinear absorption and good optical limiting measurements.

Sunita et al. [56] have studied the nonlinear optical properties of Zinc based chalcogenide thin films Zn$_x$S$_y$Se$_{100-x-y}$ for waveguide and optical fibers applications. The result shows that the values of $n_2$, $\beta_2$ and $\chi^{(3)}$ increases with the incorporation of Zn content.

Juliet T. Gopinath et al. [57] have studied the optical nonlinearity of ternary Ge-As-Se chalcogenide glass for telecommunication applications. The obtained value of $n_2$ is found to be 200-900 times higher than silica.
Yu Chen et al. [58] have reported the negative value of nonlinear refractive index of Ge-Sb-Se thin films. The ultrafast response time of the order of femtosecond make these glasses suitable for nonlinear optical devices.

The nonlinear behavior of refractive index for Ge-Se-Sb-Te chalcogenide glasses have been studied by Neha et al. [59]. The author stated that the high value of $n_2$ makes these glasses valuable for integrated optics and infrared optical sensors for medical applications.

S. Cherukulappurath et al. [60] have reported the nonlinear optical properties of quaternary chalcogenide $(\text{Ge}_{10}\text{As}_{10}\text{Se}_{80-x}\text{Te}_x$ where $x = 0, 10, 15, 20)$ glass. With the increase of Te content, $n_2$ as well as $\beta_2$ increases. The reported highest value of figure of merit (FOM) is 2.4 which is advantageous for optical limiting applications.

Pankaj et al. [61] have used Fournier and Snitzer approach for the determination of nonlinear refractive index of ternary As-Se-Ge and Bi doped As-Se-Ge chalcogenide thin films. The reported value of $n_2$ for ternary and quaternary chalcogenide thin films is found to be 2-3 order higher than pure silica. Due to high values of $n_2$, these glasses may be used as an optical material in optical fiber applications.

Sunanda et al. [45] have studied the nonlinear optical properties of chalcogenide $\text{Sb}_{10}\text{Se}_{65}\text{Ge}_{25-y}\text{In}_y$ thin films. The nonlinear refractive index increases with the incorporation of In content.

K. Petkov [62] has studied the photoinduced effect on nonlinear optical properties of various chalcogenide thin films. The result shows that value of $n_2$ is higher after UV exposure than without exposure.

The enhanced nonlinearity of chalcogenide Ge–Sb–S–Se thin films for telecommunication application has been studied by L. Petit et al. [63]. The reported value of nonlinear refractive index is found to be 500 times higher than pure silica.

1.7 Applications of chalcogenide glasses

The unique optical properties of chalcogenide glasses make them a promising material for different optical applications. A wide range of composition is available and variation in optical, thermal and mechanical properties enables these materials good among engineers from application point of view. Chalcogenide glasses are used in many applications viz; optical fibers, optical limiting devices, xerography, optical switching, remote sensing etc. The applications like memory and threshold devices are based on the thermal properties of
chalcogenide glasses. Figure 1.5 represents the applications of chalcogenide glasses. Some of the applications of chalcogenide glasses are explained below.

1.7.1 Xerography

In 1938, Carlson who discovered xerography, the first application of chalcogenide glasses in the industry. Many compositions of chalcogenide glasses like As$_2$S$_2$ and As$_2$Se$_2$ in thin film form have been used in xerography [64].

1.7.2 Infrared fiber based applications

The significant properties of infrared fibers containing chalcogenide play a vital role in various applications viz; optical biosensors, communication, imaging and laser power delivery [65]. The chalcogenide glasses fit numerous of the material necessities for these different applications [66]. As chalcogenide glasses have high refractive index, therefore they can easily be used as a core material in optical fibers. In medical field, optical fibers are used to deliver high intensity laser which is further used for many surgical techniques. Present optical fibers absorb light in mid and far infrared region and hence cannot be used for delivery of light in these wavelength regions. Power up to 3 W at 10.6 µm has been carried without damaging fibers made of Te$_2$Se$_{3.9}$As$_{3.1}$I [67]. Also, chalcogenide glasses are advantageous material for sensing the fingerprint region of bio-molecules containing proteins, nucleic acids and carbohydrates [68]. Chalcogenide fibers are used to monitor the viability of live human lung cells by recording their IR spectra, continuously after exposure to compounds inducing genotoxic or cytotoxic effects. This system can then be used to detect the presence of small quantities of toxic agents by monitoring the cell response through changes in their infrared spectra.

1.7.3 Optical limiting

Optical limiting is currently used in military to protect the sensitive detector from the high intensity lasers. The high intensity blasts from the infrared laser light can damage the sensitive detectors used for guidance and military surveillance [69]. By placing a nonlinear material in front of the sensitive detector can save the detector from the high intensity light. The material used in these devices must be transparent to laser light in wavelength of interest, but must be reacting to high intensity threats.
In addition, the high nonlinear refractive index materials are advantageous for optical limiting [70, 71]. The chalcogenide glasses have high transparency in the infrared region as well as high nonlinear refractive index, so chalcogenide glasses may be matched ideally for Nd-YAG laser operated at 10.6 μm. Accordingly, chalcogenide glasses are used as an optical limiter in optical limiting devices.

1.7.4 Optical Switching

With the expansion of fiber optic networks, the demand to switch signals between different fiber segments comes into play. Usually, this switching has been done by converting the optical signals into electrical signals and then using conventional microcircuits to route the signals onto the proper fibers. The speed of these electronic switches affects the speed of the whole optical network. To overcome this bottleneck, the
only way is to produce optical switches. For instance, Lucent Technologies currently declared an all-optical switch that permits a tenfold increase in throughput over conventional switches [72].

The nonlinear optical materials can be used in high speed performed switches to direct the signals. High-speed optical switching has been demonstrated with As$_2$S$_3$-based fibers [73-75]. Demultiplexing signals of 50 Gbit/s was attained and the system has the potential to exceed 100 Gbit/s operations [75]. A thin film optical switch must have waveguides and other optical elements to direct the flow of light to the active regions of the switch [76]. With the help of either photodarkening [77] or photodoping, waveguide can be generated using chalcogenide glasses. Other applications of chalcogenide glasses are in night vision devices, ultrafast switching, thermal imaging devices [78] etc.

1.8 Selection of the problem

Being a glass, chalcogenides are versatile platform for many technological applications. Some of the applications of chalcogenide glasses are described in above section. But recently, completely different and interesting domain of applications has been suggested in the field of electronics and optoelectronics. Because of the cheap and wide availability of silica based glasses, less attention has been given to chalcogenide glasses. But due to certain limitations of silica based devices, chalcogenide glasses become an interesting material among researchers. Recently Samsung has presented a 20 nm 1.8V 8Gb PRAM with 40 MB/s program bandwidth and Micron has announced the availability of 45 nm PCM featuring 1-gigabit (Gb) PCM plus 512-megabit (Mb) LPDDR2 in a multichip package for mobile devices - the first PRAM solution in volume production [79]. The first chalcogenide based solar cells CdTe have been used in space applications for communication satellites. The efficiency of Cu (In, Ga) Se chalcogenide is found to be 11.5% with film thickness 1-2.5 micrometer [80]. Chalcogenide glasses have been used in optical disk technology for several decades because they give fast and reproducible changes in optical properties in the presence of light [81]. These applications of chalcogenide glasses are not possible without the knowledge of the linear and nonlinear optical properties.
Among chalcogens, Se based chalcogenide glasses are of great technological importance because of their wide commercial applications. Se is vitrified as an elemental glass which is fairly stable at room temperature. The atomic number of Se is 34, indicating that it has twenty eight inner core electrons and six valence electrons in the outer most shell. The lone pair which is formed by two s-electrons does not participate in bonding. Two of the four p state electrons usually form a lone pair and are called nonbonding states and the remaining two electrons forms covalent bonding with other atoms. There is a divalent bonding in chalcogens and therefore form chain like structure. Three dimensional stability in the amorphous alloys occur due to cross linking between trigonally bonded atoms and divalent chains. The amorphous Se consists of a mixture of rings and chains constituted from trigonal and monoclinic allotropes. Besides the wide device applications like switching, memory, xerography etc. Se also exhibits a unique property of reversible transformation [82]. This property of Se makes it very useful in optical memory devices. But pure Se has some shortcomings like short life time and low sensitivity. This problem has been eliminated by alloying it with certain elements which increases the sensitivity, crystallization temperature and smaller aging effects [83]. The neutron diffraction studies of Se$_{1-x}$Te$_{1-x}$ glasses (x = 0 - 40 atomic %) states that Te has short range order and is mainly substitutional for Se [84]. There is no change in Van Der Waals bonds on addition of Te atom by isoelectric substitution because Te atom is larger than the Se atom and has more electrons in its orbital. On the addition of Te, glass transition temperature $T_g$, increases due to stronger secondary bonding and the increase in average chain mass. It also increases the concentration of charged valence alteration pair (VAP) type defects [85]. Amorphous Se–Te alloys have greater hardness, higher photosensitivity and smaller aging effects than pure Se [86]. As these glasses have poor thermo mechanical properties, in order to enlarge their domain of applications, it is necessary to increase their softening temperature and mechanical strength. The addition of third element like Bi with Se and Te, expands the glass forming area and also creates compositional and configurational disorder in the system. It also modifies the structure and thus the optical, electrical and thermal properties of the Se–Te system [87-92]. Therefore, we have selected ternary Se-Te-Bi glassy system for our study. The linear and nonlinear optical properties of this glass system have been studied in this thesis.
Chapter 1

After the pervasive study of ternary Se-Te-Bi glass system, the composition Bi$_{1.0}$Te$_{15}$Se$_{84}$ is selected as base composition for quaternary series as it possesses appreciable optical, electrical and thermal properties. It is found from the optical study that of Bi$_{1.0}$Te$_{15}$Se$_{84}$ is good because its transmission as well as refractive index is high [93]. From the electrical studies the composition with $x = 1$ is good because it possesses the highest value of photosensitivity [94]. From the thermal studies again $x = 1$ composition is good because it possesses highest crystallization temperature as well as glass forming ability [95]. The addition of element like Sn produces remarkable effect on the optical properties of chalcogenide glasses.

Muneer Ahmad et al. [51] studied the electrical and optical properties of Sn based quaternary chalcogenide glasses. Optical constants of Sn based quaternary Ge–Sb–S thin films have been studied by K.A. Aly et al. [96]. The refractive index increases while the optical band gap decreases with increasing Sn content. The enhancement in glass transition temperature with the incorporation of Sn content has been reported by Mousa M.A. Imran [97]. Effect of Sn addition on the optical parameters of thermally evaporated As–Se–Ge thin films is studied by P. Sharma et al. [46]. Refractive index has been found to increase with the addition of Sn. We have selected Sn as a fourth additive in the Se-Te-Bi base composition for our further study. After studying the linear and nonlinear optical properties of ternary Se-Te-Bi glassy system the quaternary Se-Te-Bi-Sn glass system has been explored for its linear and nonlinear optical properties.

Though some scattered literature is available on the Se-Te-Bi and Se-Te-Bi-Sn glassy alloys but many features of these compounds still remain unexplored. The aim of this study is to undertake a systematic investigation of these systems and to lighten some new features of their linear and nonlinear optical properties.

1.9 Outline of thesis

Chapter 1 describes the general introduction of amorphous semiconductors along with their different band models. A brief introduction of chalcogenide glasses as well as their linear and nonlinear optical properties has also been included. This section also includes the technological applications of chalcogenide glasses.

Chapter 2 describes the experimental techniques used for the preparation of bulk glasses, cleaning of substrate, deposition of thin films and characterization of thin films for
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X-ray diffraction. Method for optical studies of thin films using UV-Vis-NIR reflection and transmission spectra has been included. This section also includes the Z-scan technique for the characterization of nonlinear optical properties of chalcogenide thin films.

Chapter 3 explains the linear optical properties of ternary Se-Te-Bi and quaternary Se-Te-Bi-Sn thin. In the former Bi is incorporated by the simultaneous replacement of Se, whereas later includes the Sn incorporation by the replacement of Se. UV-Vis-NIR spectroscopy (reflection and transmission spectra) has been used for the analysis of linear optical properties. The refractive index and film thickness are calculated by using envelope method proposed by Swanepoel. The dispersion parameters, $E_0, E_d$ and $n_0$ are discussed in terms of Wemple-DiDomenico (WDD) model. The optical absorption in the given system seems to be of non-direct type and the optical band gap is determined in the strong absorption region by using Tauc extrapolation method. The dielectric constants and optical conductivity are determined for the system and they are found to follow the similar trend as that of refractive index.

Chapter 4 explains the characterization of nonlinear optical properties of ternary Se-Te-Bi and quaternary Se-Te-Bi-Sn chalcogenide thin films using different theoretical models. The formulation proposed by Boling, Fournier & Snitzer and Tichy & Ticha has been used to compute the nonlinear refractive index. First and third order susceptibility are evaluated using Tichy and Ticha approach in which linear refractive index and WDD parameters $(E_0, E_d)$ has been used. Two photon absorption coefficient has also been reported. The obtained results for nonlinear refractive index for both ternary Se-Te-Bi and quaternary Se-Te-Bi-Sn chalcogenide thin film is compared with pure silica, oxide glasses and other Se based chalcogenide glasses.

Chapter 5 explains the nonlinear optical properties of ternary Se-Te-Bi and quaternary Se-Te-Bi-Sn chalcogenide thin films using Z-scan technique proposed by Shaik and Bahea. Closed aperture Z-scan technique has been used for the determination of nonlinear refractive index using normalized transmission spectra and open aperture Z-scan technique has been used for the analysis of two photon absorption coefficient. The real and imaginary part of third order nonlinear optical susceptibility has also been reported.

Chapter 6 deals with the summary and overall conclusion of the work.