CHAPTER 1

Introduction
Materials science is an applied science concerned with the relationship between structure and properties of the materials. It involves examining how the microstructure of a material whether crystalline or amorphous, can be varied to influence the properties of a material. This helps in changing or enhancing inherent properties to create and improve the end products suited for use to society. Properties are divided into different categories including mechanical, electrical, thermal, magnetic, optical etc. Materials fall into one of the following classifications established by their composition and structure: metals, ceramics, polymers, composites, semiconductors, biomaterials, and nanomaterials, etc.

Matter exists in three common states of matter *i.e.* solid, liquid and gas. There is a fourth state known as plasma, ionized gas, found mostly inside stars. Solids are a particular state of condensed matter characterized by strong interactions between the constituent particles (atoms, molecules). Solids exist in either ordered (crystalline) or disordered (non-crystalline, amorphous or vitreous) state.

In the crystalline state constituent atoms or molecules are dispersed in a lattice structure having translational symmetry and can be arranged in definite structural forms. Crystalline solids can be classified into six types *viz.* metallic, ionic, network covalent, molecular non-polar, polar and hydrogen bonded. The real crystal differs from the ideal crystalline structure in terms of imperfections and defects in it. On the other hand, in non–crystalline state the constituents are not dispersed periodically *i.e.* their structural arrangement is not well defined. So, it is difficult to define a parameter that characterizes the degree of crystallinity or non–crystallinity of a solid because the possible order–disorder transitions are not unique. A typical feature of these substances is that upon heating, their viscosity drops. They gradually become soft and begin to behave like ordinary viscous liquids. Amorphous materials present a challenge and opportunity to researchers to cultivate their technological applications, since there are immense physical processes unique to these systems. These can be achieved through materials optimization and basic understanding.

1.1 Glasses

Liquid when cooled down either discontinuously solidifies to a crystalline *i.e.*, topologically ordered phase or goes through a continuous phase transition and
solidifies to a metastable disordered solid generally called amorphous phase. The liquid–crystal transition can be identified as the discontinuous drop in the volume of the system at a critical temperature with sufficiently slow quench rate. Fast quenching of the liquid mostly results in a continuous decrease in the volume when the temperature passes a threshold known as the glass transition temperature \((T_g)\). The disordered solids obtained through a glass transition are generally categorized as glasses. Glasses can be categorized in two groups: tetrahedrally coordinated silicon like materials and chalcogenide glasses.

1.1.1 Tetrahedral glasses

Tetrahedrally bonded glasses constitute fourth group amorphous semiconductors, silicon (Si) and germanium (Ge). In pure form, amorphous \((a-Si)\) and \((a-Ge)\) are formed by sputtering or thermal evaporation. Amorphous \((Si)\) and \((Ge)\) are formed by tetrahedral units, where most of the atoms have four bonds and the average bond angle is \(109.5^\circ\). Similar is the case with hydrogenated \((Si)\) \((a-Si:H)\) where hydrogen forms one bond. The \((a-Si:H)\) and its alloys have applications in large area electronic devices such as solar cells and displays.

1.1.2 Chalcogenide glasses

The word chalcogen refers to the group 16 elements \(S\), \(Se\) and \(Te\). Chalcogenide glasses are based upon these elements in binary or multicomponent systems. The four fold coordination of Si leads to the formation of highly symmetrical and rigid structures. On the other hand, two fold chalcogen leads to the formation of asymmetrical and flexible structures. Thus, the structure of chalcogenides is more complex than that of tetrahedrally bonded \((a-Si)\) or \((a-Ge)\). Chalcogenides consist of chain or layer like 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 chalcogenides are \(a-Se\), \(As_2Se_3\), \(GeSe_2\).

Chalcogenides are well known to form non–oxide glasses which have predominantly covalent bonding structures with maximum ionic conductivity of \(9\%\). Their properties vary significantly from that of oxide glasses. The thermal expansion coefficient, the temperature coefficient of the refractive index and relative
photoelastic coefficient are much higher than oxide glasses [1]. Earlier most of the studies were carried out on silicate and quartz glasses which can transmit radiation in visible region of spectrum. But, interest aroused in chalcogenide glasses as these find use in various technological applications due to their higher transparency, higher linear and non linear refractive indices, lower phonon energies etc.

Chalcogenides have lone pair and show semiconducting properties. Therefore, chalcogenides are also called lone pair semiconductors. The presence of lone pairs increase the flexibility of the bond angles which decreases the strain energy in the system. This causes the atoms to readily form amorphous structures either alone or with other constituent elements. These may be elemental like $S$, $Se$; binary $As_2S_3$, $As_2Se_3$ or in multicomponent forms as $GaSb_2Ge_{25}Se_{65}$, $Sr_2GeSb_2Se_8$. Elemental or binary chalcogenides have chain like or layered structures extending in one or two dimensions. The extent of short order is large in these glasses. On the other hand, multicomponent systems attain rigidity and a three dimensional structure and thus, have lower extent of short range order.

1.2 History of chalcogenide glasses

The amorphous materials are known since the Egyptian age for their use as glass beads. Man has been using glass in the form of silicates from thousands of years. But, the earliest experimental data on oxygen free glass have been published by Schulz – Sellack in 1870 [2]. Later on, Wood in 1902 [3], as well as Meir in 1910 [4] carried out the first researches on the optical properties of vitreous selenium. Zachariasen [5] considered the principles on how bonding requirements were met and nearest neighbor coordination maintained without imposing an exact long range order common for crystalline materials. These glasses were investigated as optoelectronic materials in infrared systems by R. Frerichs with the rediscovery of arsenic trisulfide glass in his work [6]. The earliest reference to “vitreous semiconductors” was made by Gorunova and Kolomeits in 1955 [7]. They discovered that amorphous chalcogenides are semiconductors and that the alloy $TIAsSe_2$ instead of having a crystalline structure had many properties of a typical glass. Glaze and co-workers [8] developed in 1957, the first method for the preparation of the glass at industrial scale. In 1960, Ioffe and Regel [9] realized that the bandgap depends on the existence of
short range order rather than on the long range order of the lattice and suggested that the first coordination number of corresponding crystal is preserved in amorphous structure. The glass forming region for the Si–As–Te system was planned by Hilton and Brau [10]. This development led to an exploratory DARPA–ONR program from 1962 to 1965. The ultimate goal of the program was to find infrared transmitting chalcogenide glasses with physical properties comparable to those of oxide optical glasses and a softening point of 500 °C. In 1967, Harold Hafner [11] made many important contributions including a glass casting process and a glass tempering process in Semiconductor Production Division under the direction of Charlie Jones. There work was concentrated on Ge–As–Se system [11].

In 1968, Ovshinsky [12] reported reversible phase transformation in chalcogenides, responsible for electrical switching. He produced a switching device made from an amorphous thin film of tantalum oxide, deposited on a tantalum substrate, forming one electrode while a liquid electrolyte formed a second electrode. This switch required maintaining a voltage to keep it in the high conductance state. This discovery led to the fabrication of memory devices. In early 1970’s, sensitivity of chalcogenides to light was recognized and was applied to xerography [13].

Applications of solar cells were developed by Ciureanu and Middehoek [14] and Robert and his coworkers [15]. Infrared optics applications were studied by Quiroga and Leng and their coworkers [16]. The switching device applications were introduced by Ovshinsky [12] and Bicerano and Ovshinsky [17]. P. Boolchand and his coworkers [18] discovered intermediate phase in chalcogenide glasses. Several investigators have also reported useful optoelectronics applications in infrared transmission [19, 20] and detection [21, 22] threshold and memory switching [23, 24], optical fibers [25, 26], functional elements in integrated–optic circuits [27], non–linear optics [28, 29], holographic & memory storage media [30], chemical and bio–sensors [31, 32], infrared photovoltaics [33], microsphere laser [34], active plasmonics [35], microlenses in inkjet printing [36] and other photonics [37, 38] applications.

Subsequently, several review books were published on chalcogenide glasses e.g. “The Chemistry of Glasses” by A Paul in 1982, “The Physics of Amorphous Solids” by R. Zallen in 1983 and “Physics of Amorphous Materials” by S.R. Elliott in

1.3 Band models for amorphous materials

In crystalline (c–) solids, sharp edges in density of states produce well defined forbidden band gap. This is due to perfect short range and long range order in c–solids. The a–solids have short range order. This short range order resembles with the crystalline one which implies that the concept of density of states is also applicable to a–solids. Weaire and Thorpe [39] proposed that the existence of band gap holds for a–solids, without considering the periodicity of the network. Mott first generalized the concepts of crystalline semiconductors to amorphous ones based on Anderson’s theory [40]. According to Mott, the spatial fluctuations in the potential caused by the configurational disorder in amorphous materials may lead to the formation of localized states, which do not occupy all the different energies in the band, but form a tail above and below the normal band. He further postulated that
there should be sharp boundary between the energy ranges of extended and localized states. These states are said to be localized in the sense that an electron placed in a region will not diffuse at zero temperature to other regions with corresponding potential fluctuation. There exist critical energies in each band where a sharp jump in mobility from negligible values to finite ones takes place at particular density of electronic states above which the states in amorphous solid become extended. These critical energies are called the mobility edges. The energy difference between the mobility edges of the valence band \((E_v)\) and that of conduction band \((E_c)\) is called the mobility gap. Many models have been proposed for the band structure of a–semiconductors. The main features of these models have been discussed below.

1.3.1 Cohen Fritzsche Ovshinsky model

The Cohen Fritzsche Ovshinsky (CFO) model [41] assumed that the tail states extend across the gap in a structureless distribution. The distribution of density of states \((N(E))\) for CFO model has been shown in Figure 1.1.

![Figure 1.1 Density of states for Cohen–Fritzsche–Ovshinsky model.](image_url)

They suggested that apart from the mobility edges, there are tails of the localized stated pulled out of the conduction and valence bands by disorder and there
is some overlap between these tails. Equal numbers of positive and negative charge states are produced where the tail states overlap. The overlapping bands that give rise to a finite value of $N(E)$ are due to defects of acceptor and donor type. A consequence of the band overlapping is that there are normally filled valence band states that have energies higher than empty conduction band states resulting in redistribution to restore equilibrium. In the redistribution of electrons, filled states are formed in the conduction band tails which are negatively charged and empty states are formed in the valence bands which are positively charged. This pins the Fermi level ($E_F$) close to the middle of the gap, a feature required for electrical properties of these materials. The CFO model was specially proposed for multicomponent chalcogenide glasses used in switching devices. One of the major objections against CFO model is the transparency of a chalcogenides below a well defined absorption edge leading to the conclusion that the extent of tailing is only few tenths of an electron volt in the gap [42]. Another objection to this model is that the elemental semiconductors like a–Si, a–Ge, a–As etc. should not have the extensive band tailing as they are free from compositional disorder [43].

1.3.2 Davis–Mott model

According to Davis–Mott model [44] the tails of the localized states are narrow and extend to a few tenths of an electron volt into the forbidden energy gap. The Davis–Mott band model has been shown in Figure 1.2. They proposed a band of compensated levels, originating from defects in the random network e.g. dangling bonds, vacancies etc., near the gap centre which pins the Fermi level and account for the behavior of a.c. conductivity. The band may be split into donor ($E_D$) and acceptor bands ($E_A$). Mott suggested that in making a transition from extended to localized states the mobility decreases by several orders of magnitude and a mobility edge is produced. Indeed, the concept of localized states implies that the mobility is zero at temperature ($T$) = 0K. The interval between $E_c$ and $E_v$ is defined as the mobility gap. On the other hand Cohen [42] suggested that there should be a continuous drop in the mobility, instead of an abrupt drop, occurring in the extended states just inside the mobility edge. He described the transport as Brownian motion in which carriers are
under the influence of a continuous scattering. The interpretation of electrical transport is closely related to the energy distribution of the density of states.

![Density of states for Davis–Mott model](image)

**Figure 1.2** Density of states for Davis–Mott model.

According to Davis–Mott model there are three processes responsible for conduction in amorphous semiconductors and their contribution to the total conductivity will predominate in different temperature regimes. At very low temperatures, conduction occurs by thermally assisted tunneling between states at the Fermi level. At higher temperatures, charge carriers are excited into the localized states of band tails where they can take part in the electric charge transport only by hopping. At still higher temperatures, carriers get excited across the mobility edge into the extended states. Therefore, the electrical conductivity measurements over a wide range of temperature give an idea of the electronic structure of the amorphous semiconductors.

### 1.3.3 Marshall–Owen model

A first proposal of a model showing gap was introduced by Marshall and Owen in 1971, and therefore called the Marshall–Owen model [45]. Marshall–Owen model (shown in Figure 1.3) suggested that the position of Fermi level is determined
by the well separated bands of donors and acceptors in the upper and lower halves of the mobility gap respectively. Self compensation of concentration of donors ($E_D$) and acceptors ($E_A$) takes place in such a way that the Fermi level remains near the gap centre. At low temperature, Fermi level moves to one of the impurity bands as self compensation is not likely to be complete. This model is mainly based on the observation that the high field drift mobility of $As_2Se_3$ is of Poole Frenkel type probably because of the field simulated emission of carriers from the charged trapping centers (acceptors).

![Density of states for Marshall–Owen model.](image)

**Figure 1.3** Density of states for Marshall–Owen model.

### 1.3.4 Small polaron model

The role of distortion in the presence of an extra charge carrier in an amorphous solid has been discussed in detail by Emin [46]. He suggested that if an atom is held fixed in the solid then it acts as a perturbation to its immediate environment causing a displacement of atoms in its vicinity thereby decreasing the total energy of the system. The equilibrium positions assumed by these atoms produce a potential well for the carrier. If the potential well associated with the local lattice
distortion is sufficiently deep then the carrier will occupy a bound state, being unable to move without an alteration of the positions of the neighboring atoms. This is referred to as "self-trapping." The unit comprises of the localized charge carrier and its atomic deformation is termed as small polaron when the carrier is essentially confined to a single atomic site. Since, small polaron is localized in nature so the absence of long range order in non-crystalline solids does not affect its motion.

1.4 Defect models

Defects determine the electronic and transport properties of materials which are relevant to its applications. Different models have been proposed for the defect formation in the amorphous materials which have been discussed below.

1.4.1 Mott, Davis and Street

Street and Mott [47], and Mott, Davis and Street [48], proposed a model for states in the gap of amorphous semiconductors. They considered As$_2$Se$_3$ having $10^{18}$–$10^{19}$ cm$^{-3}$ dangling bonds acting as point defects at which normal coordination cannot be satisfied. There are three dangling bond states; D$^\cdot$, containing zero electrons, D$^0$, containing one electron and D$, containing two electrons. Following Anderson [40], they assumed that a lattice distortion takes place when there is a change in the occupation of electron at dangling bonds. This distortion is sufficiently strong for reaction 2D$^0 \rightarrow$ D$^+$ + D$^-$ which is exothermic. The main objections to this model were the assumption of high density of dangling bonds and large negative effective correlation energy for chalcogenide glasses which is otherwise absent for tetrahedrally bonded amorphous materials.

1.4.2 Valence alternation pair

Kastner, Adler and Fröhlich [49] postulated the formation of valence alternation pair (VAP) which requires such a small energy of formation that their density in most of the glasses is relatively high. They proposed that each chalcogen atom in its ground state will form one positively charged three fold coordinated atom, and one negatively charged, one fold coordinated atom, i.e., $2C_3^0 \rightarrow C_3^+ + C_1^-$. In
addition to the atomic rearrangements accompanying the configuration changes, there are relaxation effects associated with a change in charge state of a given configuration [47]. VAP formation is also possible for group V atoms, but, cannot occur in group IV atoms because they cannot be fivefold coordinated.

1.5 Properties of chalcogenide glasses

By studying various properties the different aspects of the material can be studied. Physical properties are used to observe and describe materials while structural properties confirm the nature and bonding arrangement in the system. Thermal properties are characteristic of a material that determine how a material behaves when subjected to heat. Optical properties describe the response of a material when light passes through it. The aim of this section is to discuss the physical, structural, thermal and optical properties of chalcogenide glass systems.

1.5.1 Physical and structural properties

An earlier attempt to describe the structure of glasses as a disordered network of polyhedral units was made by Zachariasen [5]. The polyhedra themselves define the short-range order of the atomic arrangement in glass, whereas the random connectivity of the polyhedra gives rise to long-range disorder. Zachariasen postulated following rules for a glass forming oxide of the formula $A_mO_n$:

i. Oxygen atom may be linked to no more than two $A$ atoms.

ii. The number of oxygen atoms surrounding $A$ atoms must be small.

iii. The oxygen polyhedra share only corners with each other, neither edges nor faces.

iv. At least three corners in each polyhedron must be shared.

The crystalline and glassy structure of an oxide $A_2O_3$ has been shown in Figure 1.4. Therefore, Zachariasen defined glass as an extended network of corner sharing polyhedra which lacks periodicity and whose energy is comparable to that of corresponding crystalline network.

In order to extend the glass forming range of oxides by the addition of alkali oxides, a modified version of Zachariasen rules were formulated as [5]:

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i. A sufficient percentage of cations are surrounded by oxygen tetrahedra or triangles.

ii. The oxygen polyhedra have only corners in common.

iii. Some of the oxygen atoms are linked to only two cations and do not form any additional bonds.

![Diagram](image)

Figure 1.4 Schematic representation of (a) $\text{Al}_2\text{O}_3$ crystal (b) $\text{Al}_2\text{O}_3$ glass.

When a non–glass forming oxide like $\text{Na}_2\text{O}$ enters into the $\text{SiO}_2$ structure, additional oxygen atoms participate in the network and cause rupturing of bonds. A $\text{Si–O–Si}$ bond breaks and additional oxygen atoms saturate the $\text{Si–}$ and $\text{Si–O–}$ bonds. The oxygen which is connected to two Si atoms is called bridging oxygen and the one bonded to Si is called non–bridging oxygen. Later Warren et al. studied the structure of glass using x–ray diffraction technique and proved Zachariasen’s idea [50].

But, Zachariasen’s rules are largely inapplicable to non–oxide glasses, yet they provide a visualization of topological disorder in network forming glasses. There are two structural models based on the nearest neighbor covalent bonding, chemically ordered covalent network (COCN) [51] and random covalent network model (RCN)
which describe the structure of chalcogenide glasses more appreciably. They only differ in their approach for the formation of bonds. In COCN, for a binary species $A_xB_{1-x}$, the formation of heteropolar $A-B$ bonds is preferred over homopolar $A-A$ and $B-B$ bonds. The chemically ordered phase occurs, when only $A-B$ bonds are formed at a composition $x_c = Z_A/(Z_A + Z_B)$, where $Z_A$ and $Z_B$ are coordination numbers of $A$ and $B$ atoms respectively. If the composition is rich in element $A$ then $A-A$ bonds are also formed in addition to $A-B$ bonds and vice versa. On the other hand in random covalent network model the bond energies do not influence the formation of bonds. All the three bonds $A-A$, $B-B$ and $A-B$ are equally probable except at $x = 0$ and $x = 1$.

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. It involves the absorption measurement of different IR frequencies by a sample positioned in the path of IR beam. An IR spectrum represents fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms constituting the material. No two compounds produce same IR spectrum as each different material is a unique combination of atoms. The size of the peaks in the spectrum is a direct indication of the concentration of material present. Therefore, IR spectroscopy results in an identification of different kind of constituting materials.

Far–IR studies have been carried out on many chalcogenide systems. Kumar et al. [52] characterized the vibrational bands for $Sb_2Se_3:Sn$. Vibrational band for $Sb(Se_{1/2})_3$ at 78 cm$^{-1}$ was observed while no Sn related peaks/bands were observed in the spectra. While studying the bonding arrangement of Sn addition to SeTe alloys, a band at 222–225 cm$^{-1}$ confirmed the presence of Sn–Se bond in Sn(Se$_{1/2}$)$_4$ mode [53]. Wang et al. [54] reported that Ge–Te–In glasses present an excellent transmitting property in the Fourier Transform infrared spectra. There was no absorption in the 15–20 μm which is beneficial for far–IR transmitting applications.

Nikolic et al. [55] studied the far infrared reflectivity spectra of single crystal $PbTe$ doped with $Bi$. For strong plasma–longitudinal–optical phonon interaction, two impurity local modes at 140 and 219 cm$^{-1}$, corresponding to the impurity atom in different valence states, were reported. The lower frequency modes were assumed to be a local bismuth mode representing the population of a metastable state $Bi^{2+}$. The
other local mode at about 219 cm\(^{-1}\) was proposed to be the result of electron transfer from the stable two electron state to the conduction band. Sharma et al. [56] studied the far-infrared spectra of Ge\(_{10}\)S\(_{e90}\)Te\(_x\) glassy alloys measured in the wavenumber region 50–650 cm\(^{-1}\) at room temperature. The addition of Te in Ge\(_{10}\)S\(_{e90}\) showed the appearance of GeTe\(_2\) and GeTe\(_4\) molecular units and vibrations of Se–Te bond in S\(_{e8}\)Te\(_x\) mixed rings. Some of the Ge–Se and Se–Se bonds disappeared leading to the formation of Se Te and Ge Te bonds. For higher Te content the absorption peaks at 150 cm\(^{-1}\) were reported. The results were supported by the decrease in optical band gap with the addition of Te to Ge\(_{10}\)S\(_{e90}\) alloys.

Singh et al. [57] made IR measurements of S\(_{e98}\)Zn\(_2\)In\(_x\) (\(x = 0, 2, 4, 6, 10\)) in the wavenumber range 4000–400 cm\(^{-1}\). The transmittance percentage of FTIR recorded spectra in the wavenumber range 1800 to 400 cm\(^{-1}\) was maximum for S\(_{e98}\)Zn\(_2\)In\(_6\) glass. The IR spectra of Ge\(_{10}\)In\(_x\)S\(_{e90}\) samples was investigated by Adel et al. [58] in the wavenumber region 150–400 cm\(^{-1}\). The addition of In shifted some of the bands to higher wave numbers, and also strengthened the Se–Ge bonds. The vibrations of GeSe\(_4\) tetrahedral units were reported at 340, 270, and 220 cm\(^{-1}\). They observed that the system of Ge–Se strengthened on In addition.

Singh et al. [59] have studied the FTIR spectra in the wave number range 4000–400 cm\(^{-1}\) for S\(_{e98}\)Zn\(_2\)Te\(_5\)In\(_x\) system. The transmission percentage for S\(_{e85}\)Zn\(_2\)Te\(_5\)In\(_6\) was maximum and this composition was reported as most suitable glass of the series for prospective uses. Pamukchieva et al. [60] have studied vibrational properties of the impurities in Ge\(_3\)S\(_{b3\times3}\)S\(_{e3}\)Te\(_{10}\) bulk samples and thin films. The FTIR transmittance spectra of powdered glasses revealed that the water related impurities were dominant over the impurities of O– and C– containing complexes. The evaporated films were free from water impurities but absorption bands related to Ge–O and Te–O chemical bonds were detected, most probably due to oxidation of the surface region.

Petkov et al. [61] used the FTIR spectroscopy for studying changes in the structure of thin chalcogenide films GeSe\(_2\)–Sb\(_2\)Se\(_3\)–AgI. Two regions of absorption were observed in the IR spectra of bulk samples and thin films: the first one was situated between 225 and 325 cm\(^{-1}\) and characterized the structure of GeSe\(_2\). The second one between 125 and 225 cm\(^{-1}\) gave information about the Sb\(_2\)Se\(_3\) structure. It
was observed that the addition of iodine (I) in the GeSe$_2$ layer did not change the position of the main peak at 256 cm$^{-1}$. The intensity of the peaks at 182 and 254 cm$^{-1}$ (corresponding to the SbSe$_{6/2}$ pyramidal and the GeSe$_{4/2}$ tetrahedral units) decreased with decreasing the Ge and Sb contents in the layers, respectively. For the layer with composition of 40 at.% AgI (24 at.% I), the intensity of the peak at 205 cm$^{-1}$ increased. Dai et al. [62] studied the IR transmission spectra of Ge–Te–CuI. Although Ge Te CuI glasses are normally black and do not exhibit any transmission in the visible spectral region, but these glasses have a wide transmission window from the NIR (1.8 µm) to the far IR (25 µm). The strongest absorption peak was located at 13 µm, which was ascribed to Ge–O covalent bonds vibrations. An absorption peak was observed between 9 and 10 µm whose origin was not elucidated. These new glasses exhibited a broad optical window, lying between 1.8 and 25 µm.

Philips proposed the idea of constraint counting in network forming glasses [63]. According to Phillips, the glass forming condition for a covalent network are constrained by bond stretching ($N_d$) and bond bending ($N_b$) forces. He proposed that a mechanical threshold exists, where total number of constraints ($N_I$) equals the degrees of freedom ($N_d$) i.e., $N_I = N_d$. The composite material can be considered of as two phase materials, floppy and rigid. In the floppy regime, $N_I < N_d$ and the system is underconstrained. Conversely, in the rigid regime, $N_I > N_d$ and the system is overconstrained. Later, Philips and Thorpe [64] proposed that the rigidity threshold, describing the constraint free network with optimal glass forming ability, occurs at an average coordination number of 2.4. So, the above statement could also be postulated as, that the covalent network undergoes a qualitative change from being easily deformable at an average coordination number, $m < 2.4$ to being rigid at $m > 2.4$.

An intermediate phase in addition to floppy and rigid mode was discovered by Boolchand et al. [18]. Their results provided evidence for three distinct phases of network glasses: floppy, intermediate and rigid, as a function of progressive cross-linking or mean coordination number. The intermediate phase was characterized by a vanishing non reversing heat flow, suggesting that glass compositions in this phase were configurationally close to their liquid counterparts, i.e. self–organized. The compositional width of the intermediate phase was reported to be determined by glass structure. In random networks, the width of the intermediate
phase almost vanished, and a solitary floppy to rigid phase transition was observed, in excellent accord with extended constraint theory. According to Boolchand [18], in chalcogenides, some degree of self-organization invariably occurred. There existed an intermediate phase between the floppy and rigid phases, signaling the breakdown of mean-field constraint theory. This was in agreement with the numerical results on self-organized networks.

Lone pair electrons \((L)\) play an important role in the formation of chalcogenide glasses which can be understood in terms of valence shell electron pair repulsion theory. Zhenhua et al. [65] proposed that chemical bonds with lone-pair electrons are more flexible and thus, easier to deform. An increase in number of lone pair electrons decreases the strain energy and a structure with large number of lone pair electrons favor glass formation. However, if the number of lone pair electrons in the structure exceeds a certain limit, the vitreous state is not achieved [65]. This is because the interaction among the lone pair electrons at shorter distances is repulsive which causes steric hindrance.

Glass transition temperature \((T_g)\) is a measure of rigidity of the structure which in turn depends upon the mean coordination number \((m)\) or mean bond energy \((<E>)\). Tichy–Ticha [66] examined the correlation between the glass–transition temperature of 186 chalcogenide glasses and used the overall bond energy of the covalent glassy network by taking into account chemical bond approach as the first approximation. The bonding arrangement in the covalent network mainly determines the value of glass transition which does not mean that intermolecular interactions have no influence on glass transition. In fact these interactions play a vital role in the relaxation phenomenon in glasses.

Singh et al. [67] theoretically predicted the physical parameters of \((Se_{80}Te_{20})_{100-x}Ag_x\) \((0 < x < 4)\) glassy alloys. The mean coordination number \((m)\) increased while \(L\) decreased with an increase in Ag content. The decrease in value of \(T_g\) showed that the rigidity of the system decreased with increase in Ag content. The effect of Ge addition on the physical properties of \((Se_{80}Te_{20})_{100-x}Ge_x\) \((x = 0, 2, 4, 6)\) was studied by Mainika et al. [68]. An increase in \(m\) with increasing Ge content was correlated to an increase in the compactness of the structure. The number of lone–pairs decreased with increasing Ge due to interaction between the Ge ion and the
lone-pair electrons of bridging Se atoms. Sharma et al. [69] calculated the physical parameters of Ge$_{1-x}$Se$_{83-x}$Sb$_x$. A mechanical percolation threshold was reported at $x = 6$. With an increase in Sb content, number of lone pair electrons decreased. The value of $T_g$ increased with Ge at.% which was attributed to the formation of three dimensional structural units SbSe$_{32}$ and GeSe$_{42}$, and to the decrease of content of chain like formation of excess Se.

1.5.2 Thermal properties

Material selections for components that are exposed to excessive heat or heat fluctuations require understanding of the thermal properties and responses of materials. For example, if a material is to be used in a storage device then it should have a lower crystallization time in order to facilitate a rapid phase change. The material selection can be made by studying its thermal characteristics with time. Thus, it is important to have an insight into the thermal properties of the materials.

Figure 1.5 Schematic representation of specific volume as a function of temperature of liquid which can crystallize as well as form glass.
Glasses are formed in the process of glass transition or vitrification which is very particular in its physics, kinetics and thermodynamics. The reverse process is called devitrification which is generally, but not always, accompanied by crystallization.

Figure 1.5 shows the vitrification process for a typical liquid. The specific volume \( V_{sp} \) vs. \( T \) graph shows that a liquid may crystallize at melting temperature \( T_m \) upon cooling. This first order transition usually results in a decrease of \( V_{sp} \). On the other hand, the liquid which manages to surpass \( T_m \) without crystallization is called a supercooled liquid. As the temperature of supercooled liquid is decreased, the viscosity increases and the molecules comprising it move slowly. These arrangements are necessary to achieve equilibrium \( V_{sp} \) at that temperature. At temperatures not much lower than this, the material is practically frozen and is termed as glass [70]. The range of temperature over which this transition takes place is called the transformation range. \( V_{sp} \) continues to decrease as the temperature decreases, but the thermal expansion coefficient is significantly smaller in the glassy state as compared to liquid and supercooled liquid states. The glass transition temperature \( T_g \) is different for different cooling rates (Figure 1.6). A smaller cooling rate allows the sample to stay in the supercooled liquid state until lower temperatures. Generally, the dependence of \( T_g \) upon cooling rate is relatively weak. An order of magnitude change in cooling rate may change \( T_g \) by only 3–5 K. The supercooled liquid and the glass are considered to be metastable and unstable respectively. In contrast to a supercooled liquid, a glass relaxes continually, possibly too slowly to measure, toward a more stable state. This implies that a glass is mechanically stable for practical purposes, even though it is thermodynamically unstable [70]. A supercooled liquid may also be classified as strong or fragile [71]. Strong liquids show Arrhenius relaxation processes and have three dimensional network structures of covalent bonds. Fragile liquids follow non–Arrhenius relaxation processes and in these liquids molecules interact through non–directional and non–covalent interactions.

The crystallization of a liquid or an amorphous solid involves simultaneous nucleation and growth of crystallites [72]. The nucleation of crystals either occurs without the involvement of a foreign substance called homogeneous nucleation or with the involvement of a foreign substance acting as a preferred nucleation site.
called the heterogeneous nucleation. In order to form these nuclei two distinct barriers are to be overcome. First is the kinetic barrier and second is thermodynamic barrier [73]. The kinetic energy is the activation energy required by an atom to cross the liquid–nucleus interface. The second, thermodynamic barrier is the net free energy change in the system when a nucleus is formed. This phenomenon has been shown in Figure 1.6. It shows two different energetic contributions to the nucleation. First, a free energy decrease which is associated with the transformation of glass to a crystal (volume energy gain) and second the increase in surface energy (surface energy barrier) that inhibits the formation of the crystal. The crystal, having lower energy, is thermodynamically more stable than that in a metastable state. Hence, when the surface energy barrier is overcome, a crystal is formed.

![Figure 1.6 Energetic contributions to nucleation.](image)

The crystal growth is the successive process of nucleation in which the critical nuclei grow to form a crystal. Crystal growth takes place by fusion and re-solidification of the material i.e., molecules get arranged within a solid material in an orderly repeating pattern extending in all three spatial dimensions. In the crystal
growth process stoichiometry of the glass compositions does not undergo any compositional changes [74]. Thus, interfacial rearrangements are likely to control the crystal growth process.

The crystallization kinetics of amorphous materials is the study of crystallization with respect to time or temperature. The crystallization kinetics can be studied via isothermal or non–isothermal modes of differential scanning calorimetry (DSC)/differential thermal analysis (DTA). The kinematical studies are always associated with the activation energies generally interpreted at glass transition and crystallization. In the glass transition phenomenon, it is related to the activation energy of relaxation. The glass crystallization phenomenon is related to nucleation and growth processes which dominate the devitrification of most of the glassy systems. Although separate activation energies must be identified with individual nucleation and growth steps in a transformation, but they are usually combined into activation energy representative of the overall crystallization process. The rate of crystallization and thermal stability are the important factors to decide whether the system can be used for threshold or memory type switching.

DSC was used by Abu Sehly [75] to probe the dynamics of the glass transition in As$_{25}$S$_{75}$ chalcogenide glass. Non–isothermal measurements were performed at different heating rates (5–35 Kmin$^{-1}$). Glass transition temperature shifted to higher values with increasing heating rate. The activation energy of glass transition was calculated from the heating rate dependence of $T_g$. The observed temperature dependence of the activation energy was consistent with the free volume model of the glass transition. Crystallization studies for Se$_{0.95}$In$_{0.05}$ and Se$_{0.90}$In$_{0.10}$ were carried out by Kotkata et al. [76] under non–isothermal conditions at different heating rates. It was realized that a rate controlling process occurred where random nucleation of one– to two–dimensional growth was accompanied with the introduction of up to 10 at.% In into glassy Se matrix. The activation energy for crystallization ($E_c$) was determined using four models where a satisfactory concurrence was achieved. The value of $E_c$ showed a decrease with an increase in the In–content indicating higher extent of crystallization.

The crystallization kinetics study of Ga$_{15}$Se$_{85–x}$Ag$_x$ was carried out by Ghamdi et al. [77] using differential scanning calorimetry. The value of activation energy of
crystallization increased with an increase in Ag concentration indicating faster rate of crystallization. The glass with 8% of Ag was found to be most stable. Abu–Sehly [78] investigated the kinetics of crystallization using DSC for Se$_{81.5}$Te$_{16}$Sb$_{2.5}$. The activation energy calculated from three isothermal methods was found to vary with the extent of conversion and hence with temperature. The activation energy decreased with temperature. They showed that the transformation from amorphous to crystalline phase is a complex process involving different mechanisms of nucleation and growth.

Deepika et al. [79] employed DSC at five heating rates to investigate the glass–crystal transformation in Ge$_{1-x}$Sn$_x$Se$_{2.5}$ ($0 \leq x \leq 0.5$) under non–isothermal conditions. The glassy alloys (except 0.3) showed single glass transition and crystallization region. $T_c$ $T_g$ was found to be lowest for Ge$_{0.5}$Sn$_{0.5}$Se$_{2.5}$ showing stability in comparison to other samples. Fayek et al. [80] studied the crystallization kinetics of As$_{90}$Se$_{70-x}$Sn$_x$ ($x = 0, 1, 2, 3$) using differential thermal analysis. The average value of activation energy for glass transition ($E_g$) varied from 51.08 to 136.74 kJ/mol. Glassy alloy with $x = 2$ was found to be the most stable alloy. The glass transition behaviour and crystallization kinetics of Se$_{58}$Ge$_{42-x}$Pb$_x$ ($x = 9, 12$) was investigated using DSC [81]. The glassy systems Se$_{58}$Ge$_{33}$Pb$_9$ and Se$_{58}$Ge$_{30}$Pb$_{12}$ exhibited single $T_g$ and double crystallization on heating. From the values of $E_g$ and $E_v$, it was found that the modified phase obtained after annealing the sample, was less stable than the two phases obtained before annealing in both the samples.

Singh et al. [82] reported the non–isothermal crystallization kinetics of Se$_{98-x}$Zn$_x$In$_x$ ($0 \leq x \leq 10$) chalcogenide glasses. The activation energy showed a minimum at a composition corresponding to $x = 6$ due to a slower crystallization rate for this composition. The thermal properties of semiconducting chalcogenide Sb$_2$Se$_{55-x}$Te$_{45}$ ($2 \leq x \leq 9$) were studied by Prashanth et al. [83]. The addition of Sb was found to enhance the glass forming tendency and stability, and an increase in the glass transition width $\Delta T_g$. Glass transition temperature exhibited a subtle increase, suggesting a meager network growth with the addition of Sb. The values of $T_c$ were also observed to increase with Sb content.

Dahshan et al. [84] investigated the influence of copper addition on the thermal stability, $E_g$ and $E_v$ for Ge$_{25}$Te$_{74-x}$Cu$_x$ ($x = 2.5, 5, 7.5, 10, 12.5$) glasses. The
values of $T_g$ decreased with increasing Cu content. The composition dependence of various parameters showed an increase in thermal stability of the glasses with increasing Cu content. Shaaban et al. [85] presented the results of kinematical studies of glass transition and crystallization in glassy $Se_{85-x}Te_{15}Sb_x (x = 2, 4, 6$ and $8)$ using DSC. The activation energies, $E_g$ and $E_c$, were reported to increase with increasing $Sb$ content. An increase in $E_c$ was interpreted in terms of increasing cohesive energy. Addition of Sb turned the glasses more stable due to an increase in $Sb_2TeSe_2$ phase. Two mechanisms were reported to work simultaneously during the amorphous–crystalline transformation of the $Se_{83}Te_{15}Sb_2$ alloy while only one (three–dimensional growth) mechanism was responsible for the crystallization process of the chalcogenides $Se_{85-x}Te_{15}Sb_x (x = 4, 6$ and $8)$ glass.

Differential scanning calorimetry results for non isothermal conditions of chalcogenide ($Sb_{13}As_{30}Se_{55})_{100-x}Te_x (0 \leq x \leq 10)$ glasses were reported and discussed by Aly et al. [86]. Addition of Te resulted in decrease of $T_g$, $T_c$ and $T_m$, $E_g$ and $E_c$. The crystallization kinetics of bulk $Se_{75}Te_{15}Cd_{10}In_x (x = 0, 5, 10, 15)$ multicomponent chalcogenide glasses was studied using DSC at different heating rates (5, 10, 15 and 20 K/min) under non isothermal conditions by Kumar et al. [87]. The onset crystallization temperature, peak crystallization temperature, $E_c$ and Hruby’s parameter showed a reversal in their trend with In content at an average coordination number of 2.25. The results also showed that glassy $Se_{75}Te_{10}Cd_{10}In_5$ alloy has a maximum glass forming ability and is the most stable glass.

1.5.3 Optical properties

The optical behavior and mechanisms are very important with the use of a material for various optical applications. Optical properties describe how light interacts with the material when passes through it. Refractive index ($n$) and absorption coefficient ($\alpha$) are two important optical parameters. Refractive index is defined as the ratio of velocity of light in vacuum to velocity of light in medium. In the complex refractive index, $n^* = n - ik$, $k$ is the extinction coefficient which is related to $\alpha$. Extinction coefficient indicates the amount of absorption loss when the electromagnetic wave propagates through the material. It is a useful parameter in the engineering of optical waveguides.
Optical absorption in amorphous semiconductors can be categorized into three main regions [88], high absorption region (i) with $\alpha \geq 10^4 \text{ cm}^{-1}$ which is referred to as the fundamental absorption edge, exponential region (ii) with $1 \text{ cm}^{-1} < \alpha < 10^4 \text{ cm}^{-1}$ referred to as Urbach edge and weak absorption tail (iii) with $\alpha \leq 1 \text{ cm}^{-1}$ referred to as Urbach tail (Figure 1.7).

![Graph showing absorption spectrum of amorphous semiconductors.](image)

**Figure 1.7** Absorption spectrum of amorphous semiconductors.

Band gap is the energy needed to move a valence electron into the conduction band. When an electron undergoes transition from upper part of the valence band to the lower part of the conduction band, it causes dispersion near the fundamental absorption edge and gives rise to absorption spectrum. If this happens without the phonon participation and without a change in the crystal momentum then it is called direct transition (Figure 1.8). But, when there is interaction with phonon and a change in the crystal momentum, then it is called indirect transition (Figure 1.8). Both direct and indirect transitions give rise to frequency dependence of $\alpha$ near the fundamental absorption edge.

In high absorption region the frequency dependence of $\alpha$ is given by the power law [88],

$$\alpha \nu = B (\nu - E_{\text{opt}})^p$$  \hspace{1cm} (1.1)
where $p = 2$ for amorphous semiconductors, $B$ is a constant which depends upon the electronic transition probability and $E_g^{opt}$ is the optical band gap. In the exponential region, associated with the presence of localized states, $\alpha$ is described by [88],

$$\alpha h\nu = \text{Const.} \exp\left(\frac{h\nu}{E_s}\right)$$

where $E_s$ is the energy characterizing the slope and $\nu$ the frequency of electromagnetic radiation. In the weak absorption tail region below the exponential part, the shape depends on the preparation technique, constituent purity and thermal history of the material.

**Figure 1.8** Schematic representation of direct and indirect band gap.

Optical transmission of glasses is characterized by its optical window. At shorter wavelengths, the band gap limits the optical window, while at longer wavelengths the optical window is limited by the multi-phonon absorption. The multi-phonon absorption at longer wavelengths gives the interaction of light with vibrational modes of the chemical bonds inside the glass. The phonon energy is inversely proportional to the atomic mass of atoms. The larger atomic mass of chalcogenide elements is responsible for lower energies of phonon vibrations [89]. Chalcogenide glasses typically have optical windows that extend into the far infrared [90] making them a better candidate to be used for IR optical devices.
Introduction

The optical transmission spectra of amorphous a–Se$_{1-x}$In$_x$ films prepared by thermal evaporation technique were recorded over the spectral region of 500–2500 nm by Kotkata et al. [91]. Optical band gap decreased and refractive index increased with increasing In content. The effect of In content on the optical constants of a–Se$_{100-x}$In$_x$ thin films prepared by flash evaporation technique was investigated by Ammar et al. [92]. The value of $\alpha$ increased while $E_g^{opt}$ decreased with increase in In concentration. This behaviour was attributed to the formation of In–Se bonds and subsequent decrease in the concentration of other bonds present in the glass.

Aly [93] studied the $E_g^{opt}$ and refractive index dispersion parameters of As$_x$Se$_{70}$Te$_{30-x}$ (0 $\leq$ x $\leq$ 30) amorphous thin films deposited by thermal evaporation technique. Refractive index and dispersion energy ($E_d$) decreased while $E_g^{opt}$ and single oscillator energy ($E_0$) increased with As content. Sharma et al. [94] reported the effect of Bi addition on the optical behaviour of Ge$_{20}$Te$_{80-x}$Bi$_x$ glassy alloys. Refractive index increased with increase in Bi content. The values of $E_d$ and static refractive index ($n_0$) increased while $E_0$ decreased with Bi content. Optical bad gap decreased from 0.86 to 0.74 eV with Bi addition.

El Gendy [95] studied the refractive index and optical band gap of e beam evaporated Ga$_{10}$Ge$_{10}$Te$_{80}$ films. Optical absorption coefficient revealed the presence of an indirect optical transition for as–deposited (amorphous) films, whereas it has a direct and indirect optical transition for the annealed (crystalline) films. Sharma et al. [96] studied Ge$_{10}$Se$_{80-x}$Te$_x$ (x = 0, 10, 20, 30, 40, 50) thin films for optical properties. Optical bad gap was found to decrease with increase of Te content. The value of $n$ decreased upto x = 30 and thereafter increased with Te content.

Fouad et al. [97] studied the optical properties of As$_{30}$Se$_{70-x}$Sn$_x$ thermally evaporated thin films. The value of $E_g^{opt}$ decreased with increase in Sn content. The stoichiometric composition with x = 3 exhibited quite different behaviors as a result of the Sn alloying effect. The optical constants of Se$_{90-x}$Te$_x$Ag$_x$ (x = 0, 4, 8, 12) thin films were studied by Ghamdi [98] as a function of photon energy in the wavelength range 500–1000 nm. The value of $n$ decreased while $k$ increased with photon energy. The value of $E_g^{opt}$ increased with increase in Ag concentration. It was suggested that due to the large absorption coefficient and compositional dependence of reflection, these materials may be suitable for optical data storage.
Introduction

The compositional dependence of the optical properties of vacuum evaporated amorphous Ge$_x$Se$_{80-x}$Pb$_{20}$ films was reported by Kumar et al. [99]. Refractive index and extinction coefficient decreased at first with increasing Ge up to 20 at.% and then increased at 25 at.% Ge. Optical band gap increased with the substitution of Se for Ge up to 20 at.% and then decreased at 25 at.% Ge. Dahshan et al. [100] reported the effect of replacement of Se by Ge on the optical constants of chalcogenide Ge$_x$As$_{20}$Se$_{80-x}$ (x = 0, 5, 10, 15 and 20) thin films. The transmission spectra of the films at normal incidence were obtained in the spectral region from 400 to 2500 nm. The value of $n$ and $k$ decreased while $E_g^{opt}$ increased with Ge addition. The increase in the optical band gap with increasing Ge content was interpreted in terms of chemical–bond approach.

Marquez et al. [101] analyzed the effect of Ag content on the optical properties of Ag–photodoped a–(As$_{0.38}$S$_{0.62}$)$_{40-0.3}$Te$_x$ thin films. The value of $E_g^{opt}$ decreased with increase in the concentration of photodoped Ag. The maximum change in the index of refraction, between the Ag photodoped and undoped material, was found around 15 at.%. The optical properties of thin As$_2$S$_3$–In$_2$S$_3$ films, deposited by thermal coevaporation of As$_2$S$_3$ and In$_2$S$_3$, were reported by Todorov et al. [102]. The refractive index increased from 2.45 to 2.59, while $E_g^{opt}$ decreased from 2.40 eV to 2.18 eV for thin films with composition As$_{46}$S$_{54}$ and As$_{26.8}$S$_{60.1}$In$_{13.1}$, respectively. The addition of In leads to a decrease in the photoinduced changes in the refractive index in the visible and near-infrared region.

1.6 Motivation of thesis

There is vast spectrum of potential applications of chalcogenide glasses. But, recently an entirely different and interesting domain of applications has been proposed in the field of electronics and optoelectronics. A little attention had been paid to chalcogenide glasses because of the cheap and wide availability of silica based alternatives. However, silica based devices have certain limitations because of which chalcogenide glasses are receiving greater deal of response worldwide. Various applications of chalcogenide glasses have been realized and already been demonstrated in the fabrication of devices.
Most recently Samsung has presented a 20nm 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 [103]. A single crystal chalcogenide semiconductor $Cu_2SbSe_3$ with anomalously low thermal conductivity, 0.7–1.0 W/mK, was observed which led to its announcement as a new possible thermoelectric material by the researchers [104]. A new class of materials known as topological insulators has been introduced that are insulators in the bulk but have protected conducting surface states arising from a combination of spin–orbit interactions and time–reversal symmetry which limits possible candidates to heavy elements and rather narrow bandgap materials [105]. Some of the known chalcogenide topological insulators are $Bi_2Sb_{1-x}$, $HgTe$, $Bi_2Se_3$, $Bi_2Te_3$ and $Sb_xTe_3$ [106–108]. It has been speculated that topological insulators may be promising materials for quantum computing [109].

$CdTe$ based solar cells were the first chalcogenide based cells basically developed to be used in space applications for communications satellites. $Cu(In,Ga)Se$ based chalcogenides have a reasonable efficiency of about 11.5% with film thickness 1–2.5 μm [110] and high efficiencies approaching 19% have also been reported for laboratory scale devices by empirical optimization of process parameters [111]. Recently kesterite materials ($Cu_2ZnSn(S,Se)_4$) which are non–toxic, earth–abundant and low–cost have been proposed as alternatives [112]. Hsu et al. [113] reported superconductivity in the anti–$PbO$ type $FeSe$ at 8K. It was found that $Te$ substituted $FeSe$ and $FeSe_{1-x}Te_x$ have higher transition temperatures (~15 K) when $x = 0.5$. $FeSe_{0.5}Te_{0.5}$ coated superconducting tapes have been proposed for high field applications [114].

Metamaterials have the ability to focus and manipulate light on the nanoscale, far beyond the diffraction limit of conventional optics. Chalcogenide glasses have been used in re writable optical disk technology for several decades as they provide fast and reproducible changes in optical properties in response to excitation [115]. This functionality can be brought to bear in the metamaterials domain to create switching devices. Samson et al. [116] have demonstrated a metamaterial electro–
optic switch of nanoscale thickness based on a chalcogenide glass hybridized with a nanostructured plasmonic metamaterial.

These advances are not possible without a good understanding of different properties of the chalcogenide material. The main motive of this thesis work is to examine how the composition dependent properties (physical, structural, thermal and optical) of multicomponent chalcogenide glasses vary and can be explored for different applications.

Among S, Se and Te, S is non metal while Se and Te are metalloids (both are semiconductors). In terms of glass formation, it is very difficult to vitrify a bulk Te melt even at high cooling rates. On the other hand, selenium vitrifies as an elemental glass which is fairly stable at room temperature. Sulphur (S) based compounds are very similar to Se based glasses, but, have received less attention due to their limited transmission in mid–IR region.

Amorphous Se is known to be composed of entangled chains and/or ring molecules, depending upon the preparation conditions. Such structures are typical of organic polymers such as polyethylene because of which a–Se is generally referred to as an “inorganic polymer” [117]. Amorphous Se has a unique property of reversible phase transformation [118] making its glasses useful for memory devices. Commercially, a–Se and its alloys are used as photoconductor material in vidicon and x–ray imaging. In digital medical imaging, a–Se is used in direct conversion flat panel digital x–ray detectors. There are tremendous potential applications of a–Se based alloys [119, 120].

Amorphous Se tends to crystallize near room temperature. This temperature sensitivity limits its applications to be used as photoconductive material [121]. In order to overcome these problems, it is necessary to add more than one component like Ge, Te, Sb, As etc. into the Se matrix. Addition of Te to a–Se has shown a decrease in electrical resistivity and activation energy [122]. Sharp changes in the parameters for Te at.% > 50 have been ascribed to the phase transition from chain like structure to trigonal structure. Addition of Te decreases the $E_{g\text{opt}}$ while increases refractive index [123]. Arsenic addition increases the glass transition temperature with increasing at.% [124]. The linear refractive index was found to be maximum and $E_{g\text{opt}}$ minimum for As at.% 40 in a–Se [125]. The activation energy of crystallization
decreases as Ge is added to a–Se [126]. The defect states are minimum for \( x = 22 \) in a–Se corresponding to which activation energy and photoconductivity show a maxima [127].

In the present study, antimony (Sb) has been selected as an additive to Se because Sb improves the thermal stability of a–Se drastically and decreases the ageing effects [128]. Antimony selenide chalcogenides have orthorhombic crystal structures. SbSe system, due to its higher photosensitivity has applications in photoconductive elements [129]. Some studies have shown that a–Sb\(_2\)Se\(_3\) could also be a promising candidate for phase change memories [130]. Yoon et al. made direct comparison of antimony selenide with \( Ge_2Sb_2Te_5 \) (GST) and found that it might offer some advantages like shorter crystallization time and smaller amorphization current [131].

Shaaban et al. [132] have studied the optical properties of \( Sb_xSe_{100-x} \) for \( 5 \leq x \leq 20 \). Replacement of Se by Sb resulted in an increase in the density, \( n \) and \( k \) of these glasses while \( E_g^{opt} \) decreased with increasing Sb concentration. Sharma et. al. [128] have also reported similar variation in \( n, k \) and \( E_g^{opt} \) for \( Se_{1-x}Sb_x \) for \( x = 0, 0.025, 0.075, 0.10 \). Kushwaha et al. [129] studied the temperature and intensity dependence of photoconductivity in \( Sb_xSe_{100-x} \) thin films prepared by vacuum evaporation technique. Photosensitivity \( (\sigma_{pl} / \sigma_0) \), achieved a maximum value of 13.15 for \( Sb_xSe_{98} \).

Kostadinova et al. [133] carried out structural study of the glassy binary system \( Sb_xSe_{100-x} \) \((0 \leq x \leq 30)\). Vibrational mode \(~ 195 \text{ cm}^{-1}\) was a characteristic of Sb–Se bond in \( SbSe_{32} \) pyramidal units. Holubova et al. [134] studied the thermal and structural properties of \( Sb_xSe_{100-x} \) glass forming systems. The \( T_g \) of \( Sb_xSe_{100-x} \) changed slightly from 40 °C to 48 °C. Raman spectra confirmed that Sb–Se crystallizes from incongruent undercooled melt at lower temperature and trigonal Se crystallizes at higher temperature.

In the present study \( Sb_{10}Se_{90} \) has been chosen as the base composition. Among the studied compositions \( Sb_{10}Se_{90} \) is the best composition in terms of its ease of glass formation [135], low activation energy [129] and \( E_g^{opt} \) [128]. However, it is difficult to substitute Sb in Se for \( x > 10 \) at.\% to produce Sb–Se glassy alloys, by melt quenching technique [129]. Moreover, Sb has greater tendency to get crystallized and eutectic a–SbSe is less stable [136]. Therefore, it is necessary to add a network former (Group IV or V) such as Ge, Sn, Ag or Bi to establish cross linking between the
tetrahedral and pyramidal units which facilitate stable glass formation. The addition of Ag to Sb–Se increases the dark conductivity and is found to be activated over the entire region [137]. Adding a third element like Sn to SbSe showed an amorphous phase up to 12.5 at% of Sn while crystal structures were obtained for \( x = 15, 20, 30, 40 \) [138].

Germanium has been chosen as an additive because it increases the glass forming domain of the system which for Sb–Se–Ge system from about 5 to 40 % Sb, 5 to 35 % Ge and the rest being Se [139]. It acts as a network modifier to establish cross linking between the tetrahedral and pyramidal units which facilitate stable glass formation. Sb–Se–Ge glasses have possible applications in IR optical devices because of their low material dispersion, low light scattering and long wavelength multiphonon edge. The addition of Ge to Se–Pb system has shown that \( n \) and \( k \) are minimum while \( E_g^{opt} \) is maximum for \( x = 20 \) [140]. Similar results have been observed when Ge is added to As–Se [141] and Se–Te [142]. Increasing Ge content in Pb–Se increases the \( T_g \) and \( E_g \) of the alloys [143]. Therefore, Ge alloyed in varying concentrations \( \text{Sb}_{1-x}\text{Se}_{x}0.3\text{Ge}, (x = 0, 19, 21, 23, 25, 27) \) has been studied for physical, structural, thermal and optical characteristics.

Ge is a good glass former with Se and has a good transparency in the two spectral regions 3–5 \( \mu \text{m} \) and 8–12 \( \mu \text{m} \), but, has a disadvantage in wide energy gap which causes intrinsic optical losses, and imposes difficulties for applications in long distance fiber communication [144]. In order to overcome this limitation, the most stable of the ternary composition is taken for alloying with fourth element. Ma et al. [145] studied the Ga–Ge–Sb–Se system and found that Ga destabilizes the base system. For 5 at.% Ga samples were stable and did not crystallize. For Ga at.% > 15 the glass samples were difficult to obtain. No glass in Ga–Ge–Sb–Se was transparent in visible range while the glasses were transparent in 14–15 \( \mu \text{m} \) regions. Vassilev et al. [146] studied the addition of Pb as Pb–Se in GeSe2–Sb2Se3. With the increase in PbSe the melting temperature increased. The increase in content of PbSe at low concentration of Sb2Se3 showed a favorable effect on glass forming ability.

Indium (In) has been observed to decrease the optical band gap of the material [147], suitable to explore the system for optoelectronic devices. Sharma et al. have reported that In addition to Se–Te system increases the dark conductivity due to an
increase in the number of defects states [148]. Kumar et al. have reported that In addition to Se–Te–Cd shows a maximum for $T_c$ and $T_m$ at $x = 5$ at.% [87]. Moreover, the glass forming tendency has also been found to be maximum for same composition. Maan et al. [149] have studied the kinetics of glass transition in $Te_{5}(In_xSe_{100-x})_{95}$ glassy alloys. The value of $T_g$ increased with increasing In concentration while $\Delta E_g$ decreased and showed a minimum at $x = 20$. Currently, In has gained significant attention due to its potential applications in smart digital electronic devices [150]. These devices rely upon the non–volatile memory that uses reversible phase transition of chalcogenide resistor [150]. In based chalcogenides are also potentially used in non–linear optics in the infrared region [151]. So, in order to optimize the effect of increasing Ge concentration on different properties in ternary SbSeGe system, In has been added at the cost of Ge to the most stable of the ternary $Sb_{10}Se_{90-x}Ge_x$. The physical, structural, thermal and optical properties have been studied for varying In concentration in SbSeGeIn alloys. The thesis describes work on ternary $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) and quaternary $Sb_{10}Se_{65}Ge_{25-x}In_y$ ($y = 0, 3, 6, 9, 12, 15$) glass alloys.