Chapter 1

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Introduction

1.1 Background of Materials

Humans have been using glassy and crystalline materials for thousands of year. Many materials can exist in the amorphous, glassy phase at room temperature, even though their crystalline phase is the thermodynamically stable one. The amorphous and crystalline phases of the same material can differ substantially in their properties such as physical, electrical and thermal properties which are of great relevance to technological applications. The materials which change phase under the influence of heat, temperature and light etc are called Phase Change Materials (PCMs). They can exist in two different phases i.e. an amorphous and crystalline phase and they can be switched repeatedly between these two phases [1]. The different phases have distinctly different physical properties such as electrical conductivity, optical reflectivity, mass density, or thermal conductivity. These differences and the repeatability of the switching give these materials the ability to store information. Rewritable compact discs, digital versatile discs, and Blue-ray discs store information in thin films of PCMs, using the difference in reflectivity between the phases as the storage mechanism [2, 3].

Solids can be classified as insulators, semiconductors and conductors. Semiconductors have electrical conductivity between that of a conductors and insulators. The conductivity is an electronic process caused by the motions of electrons and holes. In 1833, Faraday reported first semiconducting property in silver sulfide. In 1873, Smith discovered the photoconductivity of the selenium and in 1876 Dams and Day reported photovoltaic effect in selenium which led to the fabrication of first photocell. The term
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‘semiconductor’ was coined by Konigsberger and Weils in 1911. Then during the Twentieth century other materials such as Si, Ge, GaAs, CdS became the interest of researches. The most important development of the semiconductor physics was the invention of Germanium based bipolar transistor in 1949 and further the silicon based field effect transistor in 1950. In 1968, Ovshinsky discovered the electronic switching based on chalcogenide glasses. After that solar cells were developed using amorphous silicon.

Amorphous semiconductors have advantages over crystalline semiconductors due to its homogeneity and isotropic nature on a microscopic scale. They are classified by the type of chemical bonding responsible for cohesive energy of the materials. The ionic materials are the halide and oxide glasses, such as transition metal oxide glasses.

Amorphous solids $V_2O_5$ and NiO have been prepared by rf-sputtering techniques. Since these materials are ionic, therefore the composition of these materials can not vary over a long range and pure materials have positional disorder. On the other hand, in the covalent materials, the presence of impurities results in transition metal ions of two different valence states. For example addition of $P_2O_5$ into $V_2O_5$ produces $V^{4+}$ ions $V^{5+}$ ions. Thus, these materials may process some degree of electronic disorder. The unsaturated transition metal ions possess spin disorder.

The covalent amorphous semiconductors can be classified as perfectly covalent bonded elemental materials such as Se, Te, S, Si, and Ge etc and binary materials such as $As_2S_3$, GeTe and chalcogenide glasses etc. The perfectly covalently bonded materials possess only positional disorder whereas binary materials possess defect states also. The
covalent amorphous semiconductors possess compositional as well as positional disorder. These disorders on the electronic band structure are responsible for the distinctive properties of these glasses and it make these materials distinct from elemental amorphous semiconductors.

Nowadays amorphous semiconductors are used in Xerography. The first material used in Xerography was amorphous selenium (a-Se) in thin film form. Recently a-Si:H films has been utilized for this purpose. The amorphous semiconductors a-Se:H is used in direct conversion of sunlight to electrical power. In 1980 C.H. Henery [4] reported the maximum efficiency of ideal photovoltaic cell reaches more than 30% for a semiconducting material with energy band gap of 1.35eV. The materials with energy band gap lying between 1eV to 2eV are considered ideal photovoltaic cells efficiency higher than 25%. The amorphous semiconductor materials are also used in fabricating of electrochemical sensor called glass electrode used to monitor the PH value of the aqueous solution [5, 6]. Glassy alloys have applications in transformer core for operation at frequencies between (50-60) Hz in transformers.

1.1.1 Crystalline and Non-Crystalline Semiconductors

Crystalline materials are solids whose constituent atoms, molecules and ions are arranged in an order or regular fashion where as in non-crystalline materials

![Figure 1.1 Arrangement of atoms in (a) crystalline and (b) non-crystalline materials](image)
constituent atoms, molecules and ions arranged randomly i.e. they lack long range order as shown in Fig.1.1

The differences between crystalline semiconductors and non-crystalline or amorphous semiconductors are as follows:

1. In crystalline semiconductors, the atoms are arranged in regular fashion in three dimensions, called long range order where as the amorphous semiconductors have no such long-range order i.e. atoms are arranged randomly.

2. In crystalline semiconductors, the chemical bonds are of definite length and angles whereas in amorphous semiconductors, the chemical bond lengths and angles may vary as atoms are arranged randomly.

3. The chemical bonds in crystalline semiconductors are chemically satisfied. However in amorphous semiconductors all chemical bonds are not chemically satisfied, called dangling bonds.

4. Crystalline semiconductors have sharp melting points. However amorphous semiconductors have no sharp melting points. In amorphous semiconductors, the transition from solid phase to liquid phase takes place within a finite time interval called softening time.

5. Crystalline semiconductors are anisotropic in nature i.e. the properties of such materials vary significantly with the direction. However the amorphous semiconductors are isotropic in nature i.e. properties of such kind of materials do not depend on the direction of measurement.

6. The energy band structures of amorphous semiconductors differ from their crystalline counterparts. In crystalline semiconductors, there exist sharp band
edges due to long range periodicity of the constituent atoms and density of electronic states at these edges sharply drops to zero. However in amorphous semiconductors, these sharp band edges are replaced by band tails and these band tails depend on the extent of disorder

1.1.2 Classification of Amorphous Semiconductors:

Amorphous semiconductors can be classified into five major categories based on their physical and chemical properties such as ionic, covalent, metallic, Vander-Waals and hydrogen. Thermodynamically, these kinds of materials are unstable and therefore they tend to relax in thermal equilibrium with time either in stable state or meta-stable state. There classifications are given in Fig. 1.2.

Ionic amorphous solids are inorganic glasses consist of mixtures of silicates with ionic bonds. These kinds of glasses have applications in glass tubing’s, widow glasses and optical instruments. This also includes halide and oxide glasses, iron phosphate and vanadium phosphate glasses. The electrical conductivity in these glasses takes place due to hopping of electrons between the ions.

The metallic amorphous solids are metal glass alloys containing metals such as Fe, Co, Ni, Al, Cr, Mn and Cu etc. together with metalloids like B, C, Si, P, N, As, and Ge etc. Apart from this, there are also earth-transition metal amorphous alloys such as GdFe, GdCo, and GdTbFe which posse’s magnetic properties.

These kinds of materials are prepared by melt-spinning and sputtering methods. These kinds of materials exhibit good magnetic properties than their crystalline counterparts.
Figure 1.2 Classifications of Amorphous Semiconductors
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Tetrahedral amorphous films belong to group IV and group III-V of the periodic table. These are prepared in thin film deposition form. The tetrahedral glasses have general formulas \( \text{A}^{II}\text{B}^{IV}\text{X}^2\text{V} \) where the suffix denotes the group in the periodic table. In these glasses the Fermi-level lies near the middle of the valence and conduction bands but some show n-type and p-type characteristics.

1.2 Chalcogenide Glasses

Chalcogenide glasses are formed from the group VI elements of the periodic table such as S, Se and Te. These elements are known as chalcogens. Chalcogenide glasses are also called Lone-pair semiconductors due to it’s distinguish characteristics of having two non-bonding p-orbital’s of the group VI elements in two fold coordination which make them unique. The conductivity of chalcogenide glasses lies between \( 10^{-13} \Omega^{-1}\text{cm}^{-1} \) to \( 10^{-3} \Omega^{-1}\text{cm}^{-1} \). They may be elemental like S, Se, Te etc or binary form such as \( \text{As}_2\text{Se}_3, \text{As}_2\text{S}_3 \) etc or cross-linked also called multi-component mixtures such as Si-Ge-As-Te, \( \text{As}_2\text{Se}_3-\text{As}_2\text{Te}_3, \text{As}-\text{Ge}-\text{Te} \) etc. The elemental and binary chalcogenide glasses have chain or layer structure with considerable order extending to locally in one-dimension or two dimensions. However the multi-component alloys or cross-linked posses three dimensional network structure. Short range orders in both elemental and binary chalcogenide glasses are longer as compared to cross-linked. The cross-linked chalcogenide have positional disorder. In 1975, Mott and his coworkers reported that the localized states in chalcogenide glasses are due to defects like those in crystalline semiconductors but not due to disorder existing in these glasses. They explained this unique property of these glasses based on the concept of dangling bonds. They have
applications in solar cells, optical switches, optical recording, image processing, IR detectors and solid state devices. During the years a new vitreous material called glassy chalcogenide material has been developed due to its attractive Infra-red properties. Chalcogenide glasses are amorphous semiconductors. They have wide applications in optical data storage and optical imaging etc.

Crystallization kinetics of chalcogenide glasses are used to determine the thermal stability and transport mechanism. The physical properties of the chalcogenide glasses depend on their atomic structure how they are arranged. The chalcogenide glasses do not retain their atomic structure in the influence of external factors such as heat, light energy and composition etc. The study of crystallization kinetics is helpful in analyzing the switching behavior of these glasses which depends on the rate of crystallization.

Many researchers have done work on chalcogenide glasses. Amorphous semiconductors which contain one or more chalcogenide such as S, Se, and Te etc are called chalcogenide glasses. Se-based chalcogenide glasses have wide applications in switching, memory devices, xerography and photo cells etc. Since pure selenium has short lifetime and low sensitivity, therefore it is mixed with impurity atom such as In, S, Sb, Bi etc to make it more robust, high crystallization temperature, high sensitivity and smaller aging effects. The addition of impurity atoms make compositional disorder and widen the glass forming area. In my research work I have reported the crystallization kinetics of In-Se-S ternary and quaternary In-Te-Bi-Se chalcogenide glasses by Non-isothermal method.
In 1960, B.T. Kolomiets [7] and his coworkers reported that glasses containing chalcogen elements such as Se, Te, and S could act as semiconductors. In 1975, W.E. Spear [8] published his work on the drift mobility in vitreous selenium.

In 1966, J. Tauc et al [9] reported their studies on amorphous Germanium. In 1968, S.R Ovshinsky [10] reported his work on threshold and memory switches in chalcogenide glasses. He showed his work on the use of chalcogenide thin films in computer memory. In 1975, W.E. Spear and P.G Le Comber [11] developed a technology n-type and p-type amorphous silicon semiconductor similar to crystalline semiconductor. Glassy metallic alloys have advantage over their crystalline counterparts in varying the magnetic properties of the materials such as Curie temperature, magnetization etc by changing the composition the alloys. Therefore, amorphous semiconductors are used in magnetic sensors. The optical studies of the amorphous semiconductors are useful in fabricating the optoelectronic devices. The optical absorption spectra of the semiconductors exhibits threshold light can pass through the material without any loss below a particular frequency called the threshold frequency and above the threshold frequency, lights are absorbed. Amorphous semiconductors have good luminescence properties in the visible and infrared regions.

The structural properties of the amorphous semiconductors are characterized by the bond length, bond angle, coordination no., etc. Amorphous semiconductor materials do not have a definite melting point. The phase transition from solid to liquid takes place at a temperature greater than the glass transition temperature. The physical properties of the amorphous semiconductors determine its technological applications in the field of solid
state devices. This physical property more or less depends on the composition of the alloys. They have wide applications in the electronic and optical switches, optical recording media, and IR detectors, photo darkening or bleaching and inorganic resists [12-18]. Crystallization kinetics of amorphous semiconductors determines the rate of crystallization, activation energy, transition temperature and crystallization temperature etc.

Many researchers have studies [19-23] thin films of amorphous chalcogenide glasses and its application as a phase change material. The optical study of thin films determine the reflectance, optical absorption, refractive index and extinction coefficient. They are called optical constants. These optical constants change under the influence of light, heat and composition.

Chalcogenide glasses are inorganic glassy material containing one or more chalcogen element such as Se, Te and S. Chalcogenide glasses are less robust and weakly bonded than oxide glasses. The first commercially developed chalcogenide glass was As$_2$S$_3$. In 1950, S.R. Ovshinsky [24] developed a computer memory based on chalcogenide glasses. Doping of Bismuth in Ge-Se chalcogenide glasses shows n-type conduction. The phase transition in chalcogenide glasses is a unique property which can be exploited in optical memory applications.

1.3 Glass Transition

A glass is an amorphous solid which exhibits glass transition. The glass transition is a phenomenon in which crystal undergoes liquid phase with the increase in temperature and consequently thermodynamic properties such as heat capacity changes.
When a liquid is cooled then either crystallization takes place at melting point $T_m$ or it undergoes a super cooled state below $T_m$ and with decreasing temperature its viscosity increase and consequently form a glasses as shown in Fig. 1.3.

The crystallization process occurs due to abruptly change in volume at $T_m$ whereas the glass formation is characterized by a gradual break in slope. The region over which the change of slope occurs, is called as ‘glass transition temperature’ $T_g$ it is found that the slower the rate of cooling, the larger is the region for which the liquid may be super cooled and hence the lower glass transition temperature.

The thermal relaxation is a process in which a glassy substance following an abruptly change in temperature during the quenching process at $0^\circ$ C cooled water, relaxes from a state of higher enthalpy to an equilibrium state of low enthalpy.
1.4 Properties of Chalcogenide Glasses

Selenium based chalcogenide glasses have commercial importance. Amorphous Selenium has been investigated extensively. Se is a Group VI element and therefore it requires only two nearest neighbors to fulfill its bonding requirements as compared to Ge and Si. One advantage of Se over Si and Ge is that amorphous Se can be quenched from the liquid state and bulk glassy samples can be made. Se has a complicating feature because it crystallizes in two different structures [25]. The stable form below the melting point (493K) is trigonal, and atoms being arranged in spiral chains so that the projection on a plane perpendicular to the axis is an equilateral triangle. The intrachain bonding is covalent while the interchain bonding is because of relatively weaker Vander Waals attraction. The structure is highly anisotropic. Two metastable monoclinic forms of Se exist such as $\alpha$-monoclinic Se and $\beta$-monoclinic Se [26-27]. The principle structural unit in both structures is not infinite long chains of Se but finite molecules in the form of puckered Se$_8$ rings. Thus monoclinic Se is molecular (or monomeric) rather than polymeric. The intramolecular bonding is covalent, the intermolecular forces are Vander Waals. In all three forms of crystalline Se, the covalent bond length is the same ($\sim 2.32$ Å). In addition, the bond angles ($105^0$ in the trigonal form) are only slightly distorted ($\sim \pm 4^0$) in the monoclinic forms. The closest Vander Waals separations in the three structures are equal ($\sim 3.5$ Å). Since Se is intermediate between S and Te in the periodic table, therefore the monoclinic Se has very similar structural as orthorhombic S (which contains molecular S$_8$ rings) where as trigonal Se has the same structure as crystalline Te. Amorphous Se consists of both Se$_8$ rings and polymeric Se chains, It is reported that some amount of rings and chains is temperature. Since Se8 rings are disjoint therefore, amorphous Se is not a random-network glass like amorphous Ge and Si. This happens because Se is a partially covalent and partially Vander Waals material.
whereas Ge and Si are totally covalent. A purely covalently bound random network of Se atoms cannot fill three-dimensional space [28].

The mobility gap and density of states of amorphous Se are approximately 2.1 eV. This indicates that extensive band tails due to positional disorder do not exist. This signifies that the potential fluctuations are not very large. This explanations that Se-Se bond lengths and the bond angles in the monoclinic forms and trigonal of Se are similar. Thus the short-range order in monoclinic Se, trigonal Se and amorphous Se are equivalent. This has been experimentally established by the optical absorption of these materials.

Although Chalcogenide glasses (containing Se,Te and S etc) have been studied for more than one hundred year [29] but the intensive investigation of these glasses started only after the discovery these materials transmit light in the infrared region [30-32]. Research on the multicomponent chalcogenide glasses was impelled by the discovery that multicomponent glass Tl2Se-As2Se3 possessed semiconducting electrical properties and its conductivity is of the order of $10^{-9} \, \Omega^{-1} \, \text{cm}^{-1}$ at room temperature [33-34]. After this in 1960 B.T.Kolomiet and T.F. Nazarova [35] that amorphous Tl2Se.As2Te3 had conductivity $\sim 10^{-3} \, \Omega^{-1} \, \text{cm}^{-1}$ at room temperature which is larger than many crystalline semiconductors. This discovery led to investigation of ternary and quaternary chalcogenide alloys. Many researchers have reported glass formation and physical properties of ternary and quaternary chalcogenide glasses [36-41].

1.4.1 Structural Properties

The structural properties of amorphous materials depend on the structural arrangement of atoms. Chalcogenide glasses can be characterized by short range order and partially intermediate range order. Zachariasen [42] reported the first significant explanation of
the amorphous material structure. The diffraction pattern of amorphous materials consists of broad halos rather than sharp peaks as appears in Bragg’s reflection. A small crystallite size having imperfections and strains gets widen normal to the sharp crystalline reflections. As the crystal size gets smaller and a point is reached where crystalline reflection overlaps and the diffraction pattern appears to be amorphous. Many authors [43-44] have reported this phenomenon of crystallite size at which the diffraction pattern appears to be amorphous. Although the atomic structure of chalcogenide glasses lacks long range translational periodicity but due to chemical bonding, the characteristic glasses do possess high degree of short range order symmetry with respect to atomic polyhedral [45]. Chalcogenide glasses have the properties in between oxide glasses having three dimensional network and organic polymers having one dimensional chain structure because chalcogens (Se,Te and S etc) and oxygen both belong to Group VI of the periodic table [46]. In chalcogenide glasses, the atomic bonding is more flexible than oxide glasses and more rigid than organic polymers.

There are different structural models to explain the structure of amorphous materials. These structural models are given below:

(a) The Continuous Random Network (CRN) model: In this model it is assumed that atoms having coordination numbers greater than or equal to four are associated by covalent bonds [42]. It has given understanding of covalent bonds in amorphous silicon (a - Si), amorphous silica (a – SiO$_2$) and a – As$_2$Se$_3$. The local atomic structure in amorphous materials is not completely random but it has some degree of short range order. All covalent bonds of each atom are saturated i.e. coordination of the constituent atoms satisfies the 8 – N Rule, where N represents the column in the periodic table to which the element belongs to [47]. This model is found to be applicable in bulk
quenched glasses and annealed thin films. This model does not admit any defects such as dangling bonds (unsaturated) or over-coordinated.

(b) The Random Close Packing (RCP) model: It is also called Dense Random Packed (RCP) model. These models are useful in studying the structure of metallic glasses [46] such as nickel–phosphorous (Ni-P), copper–zirconium (Cu-Zr) and gold–silicon (Au–Si) alloys etc.

(c) The Random Covalent Network (RCN) model: This model has been proposed to explain the local structure of amorphous semiconductors [48]. This is the extension of CRN model. The effect of short range order and medium range orders on the structural properties of amorphous materials have been discussed [49-51].

In most of the binary alloys except GeTe, the short-range order of the amorphous and its counterpart crystalline materials is the same. However, in the pseudo binary As₂Se₃-As₂Te₃ system, Vaipolin and Porai-Koshits [52] reported some differences in short range order. They interpreted these differences in terms of relative covalency and iconicity of the constituent bonds. The Study on the structure of PbS-As₂Se₃ system led to the conclusion that As₂Se₃-rich glasses are similar in structure to that of amorphous As₂Se₃ [53]. The PbS-rich glasses resembled PbS itself due to equivalence of short-range order in amorphous and its counterpart crystalline materials.

Since a covalently bound material is very resistant to crystallization, therefore, it being a first hypothesis to assume that the multicomponent chalcogenide glasses are covalent in nature and its all bonding requirements of each constituent atom is locally satisfied. Agarwal and Fritzsche [54-55] reported a spin density of \( \sim 10^{15}-10^{16} \text{ cm}^{-3} \) in chalcogenide glasses depending on the thermal stability of the material.

The chemical structure that constitute short range order and long range order are obtained by using X-rays, electrons and neutron beams. Extended X-ray absorption fine
structure (EXAFS) is a probe particularly sensitivity for investigating the local structure around the atoms. The morphology of the samples and the inhomogeneity present in the form of phase separation and voids can be examined by transmission electron microscopes (TEM) and scanning electron microscope (SEM). Composition of constituent elements present in the amorphous materials is studied by Energy Dispersive X-rays Spectroscopy (EDS). The Raman and Infra-red Spectroscopy are used to examine the degree of disorder and chemical bonding. The medium range of amorphous network can be well understood by small angle scattering.

The structural properties of ternary and quaternary chalcogenide glasses have been reported by several authors [56-59].

Kumar et al [56] studied the structural properties of Se$_{80-x}$Te$_{20}$Sn$_x$ ($0 \leq x \leq 10$). The XRD pattern of an as-prepared sample of ternary Se$_{76}$Te$_{20}$Sn$_4$ alloy does not show any sharp peak. Therefore, it confirms the amorphous nature of the alloy.

Mohsin Ganaie and M Zulfequar [57] reported the structural properties of Cd$_4$Se$_{96-x}$S$_x$ ($x = 4, 8$ and $12$). They have carried out the structural properties of the by XRD, FTIR, SEM and Raman Spectroscopy. It was found that XRD pattern of the prepared films are in nanoscale region having polycrystalline nature with preferred orientation along (002) plan and hence confirms the amorphous nature of thin films.

Ashraf et al [58] reported the structural properties of In$_4$Se$_{96-x}$S$_x$ ($x = 0, 4, 8$ and $12$) thin films. They studied structural properties by XRD, SEM and EDS. XRD patterns show no sharp peak hence it is amorphous in nature. SEM reflects the development of grains and EDS analysis shows the presence of composition of constituent elements in the thin films.
Singh et al [59] have investigated the structural properties of bulk \( \text{Se}_{93-x}\text{Zn}_2\text{Te}_5\text{In}_x \) \((x=0, 2, 4, 6 \text{ and } 10)\) chalcogenide glasses. The concentration dependence structural phenomena of the alloys have been explained with help of average coordination number.

### 1.4.2 Thermal Properties

Thermal properties of the ternary and quaternary chalcogenide glasses give the information about crystallization kinetics. It gives the inputs of various reactions that take place during the heating of the material. Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) have been used to study glass transition behavior such as glass transition temperature \((T_g)\), crystallization temperature \((T_c)\), melting temperature \((T_m)\) and enthalpy of crystallization etc and other thermodynamic properties such activation energy for crystallization \((\Delta E_c)\) and activation energy for structural relaxation \((\Delta E_t)\) etc.

K.A.Aly et al. [60] have reported the crystallization kinetics of \( \text{Bi}_x(\text{Se}_{20}\text{Te}_{80})_{100-x} \) under non-isothermal condition using DSC. These glasses were synthesized by melt quench technique. Thermal stability decreases with increasing the bismuth content. Both the heating rate and Bi content are found to affect the values of the characteristic temperatures such as the glass transition temperature \((T_g)\), the peak temperature of crystallization \((T_p)\) and the melting temperature \((T_m)\). The activation energy for glass transition \((E_t)\) and for crystallization \((E_c)\) were deduced.

Sunil Kumar and Kedar Nath [61] studied the glass transition kinetics of glassy \( \text{Se}_{90-x}\text{Te}_5\text{Sn}_5\text{In}_x \) \((x = 0, 3, 6 \text{ and } 9)\) using DSC under non-isothermal conditions at different heating rates 5, 10, 15 and 20 K/min. They observed that in these glasses, the
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glass transition temperature ($T_g$) is found to be dependent on composition and heating rates. The glass transition activation energy ($E_g$) was found to be minimum at 9 at % of In. The thermal stability increases on the addition of In to ternary $\text{Se}_{90}\text{Te}_5\text{Sn}_5$ glass.

A. M. Abd Elnaeim et al. [62] have reported glass transition and crystallization kinetics of $\text{In}_x(\text{Se}_{0.75}\text{Te}_{0.25})_{100-x}$ using DSC under non isothermal conditions.

The composition dependence of the glass transition temperature ($T_g$), crystallization temperature ($T_c$), activation energy for glass transition ($E_t$) and activation energy for crystallization ($E_c$) were discussed in terms of the chemical bond approach.

Jun HoLee et al. [63] studied the thermal properties of ternary Ge-Sb-Se chalcogenide glasses for use in molded lens applications. Compositional dependence of glass transition ($T_g$) and crystallization temperature ($T_c$) were evaluated. It is found that the glass structure becomes energetically more stable and topologically more connected with increasing Ge content and thermal properties are closely connected with mean coordination number and average bond energy.

A.A.Al-Ghamdi et al. [64] studied the crystallization kinetics of chalcogenide glasses $\text{Ga}_{15}\text{Se}_{85-x}\text{Ag}_x (x = 0, 2, 4, 6$ and $8)$ for use in optical memory devices and holography etc. under non isothermal conditions using DSC. They prepared these bulk alloys by melt quenching technique. On the basis of the obtained experimental data, they reported that the temperature difference ($T_c - T_g$) and the enthalpy released ($\Delta H_c$) are found to be maximum and minimum, respectively, for $\text{Ga}_{15}\text{Se}_{77}\text{Ag}_8$ glass, which indicate that this glass is thermally most stable in the composition range under investigation.

Omar A.Lafi et al. [65] have reported the compositional dependence of thermal stability of $\text{Se}_{90}\text{Te}_{10-x}\text{Sn}_x (x = 2, 4, 6$ and $8)$ chalcogenide glasses. They observed that thermal stability and glass forming ability exhibit a maximum at $x = 4$ at % of Sn.
F.A. Al-Agel et al. [66] studied the crystallization kinetics of $\text{Ga}_{10}\text{Se}_{87}\text{Pb}_3$ and $\text{Ga}_{10}\text{Se}_{84}\text{Pb}_6$ using DSC under non-isothermal conditions at constant heating rates of 5, 10, 15, 20, 25 and 30 K/min. The glass transition temperature ($T_g$), crystallization temperature ($T_c$), and melting temperature ($T_m$) were determined from DSC thermograms. They observed that Enthalpy released is found to be maximum for $\text{Ga}_{10}\text{Se}_{87}\text{Pb}_3$ as compared to $\text{Ga}_{10}\text{Se}_{84}\text{Pb}_6$.

Anis Ahmad et al. [67] have investigated the crystallization kinetics of $\text{Se}_{80}\text{Te}_{20-x}\text{Zn}_x$ with $x = 0.5, 1.0, 1.5, 2.0$ and 2.5 chalcogenide glasses using DSC under non-isothermal conditions. It was found that the enthalpy released is minimum at 2.5% of Zn; hence the glass with 2.5% of Zn is most stable in the $\text{Se}_{80}\text{Te}_{20-x}\text{Zn}_x$ system.

Neha Sharma et al. [68] reported the thermal analysis of quaternary Ge-Se-Sb-Te chalcogenide alloys. $\text{Ge}_{19-y}\text{Se}_{63.8}\text{Sb}_{17.2}\text{Te}_y$ ($y = 0, 2, 4, 6, 8, 10$ at %) synthesized using melt quench technique. Glass transition and crystallization kinetics of alloys was investigated using DSC at different heating rates (5, 10, 15, and 20 K min$^{-1}$). They observed that values of both glass transition temperature ($T_g$) and crystallization temperature ($T_c$) increase with increasing heating rate but decrease with Te content. The glass transition activation energy ($\Delta E_t$) decreases with increasing concentration of Te content.

A. Dahshan et al. [69] characterized the $\text{Ge}_{20}\text{Se}_{60}\text{Sb}_{20-x}\text{Ag}_x$ (where $x = 0, 5, 10, 15$ and 20 at %) chalcogenide glasses. They reported that glass transition temperature ($T_g$) decreases while the cohesive energy and the overall mean bond energy increase with increasing Ag content. The increasing cohesive energy with an increase of the Ag content interpreted on the basis of chemical bond approach.
A. Kumar et al. [70] studied the crystallization kinetics of Se$_{80.5}$Bi$_{1.5}$Te$_{18-y}$Ag$_y$ (for $y = 0, 1.0, 1.5,$ and $2.0$ at %) chalcogenide glassy alloys using DSC. They found that thermal stability and the glass forming ability increase with the increasing concentration of Ag. This is attributed to an increase in the cohesive energy. From the study it was observed that Se$_{80.5}$Bi$_{1.5}$Te$_{16}$Ag$_2$ composition is thermally more stable.

A.K.Singh et al [71] reported the thermal stability and glass forming ability of Se$_{93-x}$Zn$_2$Te$_5$In$_x$ ($0 \leq x \leq 10$) chalcogenide glasses using DSC under non isothermal condition. They observed a significant variation in glass forming ability and thermal stability with indium content.

S.Kumar et al. [72] studied the crystallization kinetics of quaternary chalcogenide glasses Se$_{75}$Te$_{15-x}$Cd$_{10}$In$_x$ ($x = 0, 5, 10$ and $15$) at different heating rates ($5, 10, 15$ and $20 \, ^0\text{K/min}$) under non isothermal conditions. They used DSC technique to determine the various kinetic parameters of crystallization. They reported that glassy Se$_{75}$Te$_{10}$Cd$_{10}$In$_5$ alloy has a maximum glass forming ability and is the most stable glass.

S. Sharda et al. [73] studied the thermal stability and crystallization kinetics of quaternary Sb$_{10}$Se$_{65}$Ge$_{25-y}$In$_y$ ($y = 0, 3, 6, 9, 12$ and $15$) using DTA under non isothermal condition at different heating rates ($5, 10, 15$ and $20 \, ^0\text{K/min}$). Heating rate dependent of $T_g$, $T_c$ and $T_m$ decrease with increasing In content while activation energy of crystallization ($E_c$) decreases. This is due to the replacement of higher energy Ge–Se bonds with low energy In–Se bonds and therefore formation of homopolar Se–Se bonds.
1.4.3 Optical Properties

Chalcogenide glasses are the promising candidates for the photonic application owing to their interesting optical properties like high absorption coefficient, high efficiency of radiative recombination, high photosensitivity and nearly matching band gaps in ultraviolet and visible region of solar spectrum. The design and realization of optical components based on these materials requires detailed information on their optical properties like electronic band structure, optical transition, opto-electronic behavior and transport of charge carriers etc. The band gap represents the minimum energy difference between the top of valence band and the bottom of conduction band.

Optical-absorption spectra of chalcogenide glasses exhibits relatively sharp absorption edges from which optical gaps can be deduced [74-76]. The optical gaps obtained for multi-component chalcogenide glasses are always approximately twice the activation energy for electrical conduction in view of apparent pinning of the Fermi energy. According to Cohen, Fritzsche and Ovshinsky (CFO) Model, the fermi energy should always be near the center of mobility gap if the balance and conduction bands tail symmetrically. The temperature coefficient of the optical edge of chalcogenide glasses lies between $4 \times 10^{-4}$ eV/K and $-10 \times 10^{-4}$ eV/K as its counterpart crystalline semiconductors [77-79]. Fagen and Fritzsche [76] studied electro-absorption of thin films of quaternary chalcogenide glasses $\text{As}_{35}\text{Te}_{28}\text{S}_{21}\text{Ge}_{16}$ at 77K, and they observed a small shift, of the order of $3 \times 10^{-15}$ eV-cm$^2$/V$^2$, comparable to room temperature value observed in amorphous Se but smaller than that for crystalline Se or CdS by approximately factor 100 [80-83].
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R.K. Pan et al. [84] reported chalcogenide \((\text{GeSe}_2)_{100-x}\text{Bi}_x\) \((x = 0, 0.4, 2, \text{ and } 4)\) thin films deposited by the pulsed laser deposition technique. The optical transmission spectra, absorption spectra of the films have been used to calculate optical parameters. The transmission spectrum found to shift towards longer wavelength while refractive index increases with increasing Bi concentration. The optical band gap \((E_g)\) decreases with addition of bismuth.

D.K. Dwivedi et al. [85] investigated the optical properties of \(\text{Se}_{75-x}\text{Te}_{25}\text{In}_x\) \((x=0, 3, 6, 9)\) chalcogenide thin films prepared by thermal evaporation technique under vacuum. The absorption spectra measured in the spectral range 400-1100 nm for the optical characterization of thin films. They reported that the absorption coefficient \((\alpha)\) increases with the increase in incident photon energy and with increasing indium concentration. Optical band gap \((E_g)\) also decreases with increasing indium concentration in glassy system.

H. Nyakotyo et al. [86] investigated the effect of annealing on optical properties of \(\text{Se}_{79}\text{Te}_{10}\text{Sb}_4\text{Bi}_7\) chalcogenide thin films prepared by Electron beam deposition technique. The optical transmission of these films studied in the range 300–2500 nm. They reported that optical band gap \((E_g)\) optical decreases with increasing annealing temperature in the range 333–393 K. Other optical parameters such as Urbach energy \((E_u)\), optical conductivity \((\sigma_{opt})\), real and imaginary part of dielectric constant \((\varepsilon_i, \varepsilon_r)\) change with increasing annealing temperature.

E.R. Shaaban et al. [87] reported the optical properties of \(\text{Se}_{80-x}\text{Te}_{20}\text{Bi}_x\) \((x = 0, 2, 4, 6, \text{ and } 8)\) thin films. Thin films deposited by evaporation technique and optical properties were investigated in the spectral wavelength range of 400 – 2500 nm. They observed that the
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refractive index increases with increasing the concentration of Bi in the bulk system of alloys. The optical transition was found to be allowed indirect with optical energy (\(E_g\)) decreases from 1.467 to 1.035 eV with increasing Bi concentration.

K. Sharma et al. [88] investigated the optical properties of \(\text{Se}_{80-x}\text{Te}_{20}\text{Bi}_x\) \((x = 0, 2, 4, 6\) and 8) amorphous thin films. They reported that optical band gap decreases with increasing bismuth concentration while optical band gap (\(E_g\)) decreases. Austine A. Mulama et al. [89] investigated optical properties of \(\text{Se}_{85-x}\text{Te}_{15}\text{Sb}_x\) \((x = 0.0, 0.5, 2.5\) and 5.0) chalogenide thin films deposited by flash evaporation technique. They reported that on increasing concentration of antimony, absorption coefficient increases. While the optical band gap (\(E_g\)) energy decreases.

Deepika and Hukum Singh [90] investigated the optical properties of nano structured \(\text{Se}_{80-x}\text{Te}_{20}\text{Sb}_x\) thin films prepared by inert gas consolidation method. They reported that optical band gap (\(E_g\)) decreases with increasing antimony concentration while refractive index (n) increases. R.P.Tripathi et al. [91] investigated the thickness dependent optical properties of \(\text{Se}_{85}\text{In}_{12}\text{Bi}_3\) nanochalcogenide thin film. They reported absorption coefficient (\(\alpha\)) and extinction coefficient (\(k\)) increases with photon energy and decreases with film thickness. The optical transition was found to be allowed and indirect. Pankaj Sharma et al. [92] reported the optical properties of quaternary chalcogenide \(\text{Ge}_{20}\text{Se}_{60}\text{Sb}_{20-x}\text{Ag}_x\) \((x = 0, 5, 10, 15\) and 20) thin films prepared by thermal evaporation technique. The optical properties were investigated in the spectral wavelength range of 400 – 2500 nm. They observed that the increasing concentration of silver the refractive index (n) decrease from 2.71 to 2.49 while the optical band gap (\(E_g\)) increases from 1.37 to 1.55 eV.
In multicomponent chalcogenide glasses, the electrical conductivity increases exponentially with increasing temperature in accordance with the ordinary semiconductor expression as

\[ \sigma = \sigma_0 \exp \left( -\frac{\Delta E}{kT} \right) \]  

(1.1)

Where, \( \sigma_0 \) is pre exponential factor, \( \Delta E \) is activation energy, \( k \) is Boltzmann constant and \( T \) is temperature.

The typical value of \( \sigma_0 \) lies between \( 10^2 \, \Omega^{-1} \, \text{cm}^{-1} \) and \( 10^4 \, \Omega^{-1} \, \text{cm}^{-1} \) and \( \Delta E \) from 0.3 to 1.0 eV range [93-95]. The sharp increases in the apparent activation energy (\( \Delta E \)) (the slope of plot ln \( \sigma \) vs l/T) can occur at temperatures lying between the glass transition temperature and the melting point [96-97]. The intrinsic conduction that characterizes liquid Se, the activation energy is about 1.1eV. This behavior extrapolated to low temperatures shows the observed electrical conductivity of very pure amorphous Se.

Intrinsic conduction can also be observed in compensated amorphous Se. The room-temperature conductivity is about \( 10^{17} \, \Omega^{-1} \, \text{cm}^{-1} \). The mobility of free holes in the valence band dominates that of free electrons in the conduction band. The free-hole mobility may be of the order of 20 cm²/V-sec. The holes conduction is predominantly band-like. The drift mobility is trap-limited, and the traps are most likely the acceptor levels. The hopping conduction can be observed in ac conductivity experiments. This conduction probably occurs within the acceptor levels rather than in any intrinsic localized states. The density of states at the fermi energy is of order of \( 10^{18} \, \text{cm}^{-3}/\text{eV} \) [98].
M. A. Afifi et al. [99] investigated the electrical properties of chalcogenide Se\textsubscript{75}Ge\textsubscript{25}\textsubscript{x}Sb\textsubscript{x} thin films. They reported that electrical conductivity (σ) increases while the activation energy (ΔE) and pre-exponential factor (σ\textsubscript{0}) both decrease with increasing concentration of antimony. F.A. Al-Agel et al. [100] reported the effect of annealing temperature on electrical properties of chalcogenide Ga\textsubscript{15}Se\textsubscript{77}In\textsubscript{8} thin films. They observed that conduction is due to thermally assisted tunneling of the carriers in the localized states near the band edges. The dc conductivity (σ) increases while activation energy (ΔE) decreases on increasing annealing temperature. I. S. Ram et al. [101] investigated the electrical conductivity of Se\textsubscript{90-x}Te\textsubscript{5}Sn\textsubscript{5}In\textsubscript{x} (x = 0, 3, 6 and 9) chalcogenide thin films. They observed that activation energy (ΔE) and pre exponential factor (σ\textsubscript{0}) both increase with the increasing concentration of indium varied from 0.091 to 0.194 eV.

Z. H. Khan et al. [102] investigated the dc conductivity of Se\textsubscript{80-x}Ge\textsubscript{20}In\textsubscript{x} (x = 0, 5, 10, 15 and 20) thin films. They observed that activation energy (ΔE) decreases with the increasing indium concentration up to 10% and then starts increasing at higher concentration. M. A. M. Khan et al. [103] investigated the dc conductivity of Se\textsubscript{78.5}Te\textsubscript{22}Bi\textsubscript{x} (x = 0, 0.5, 2 and 4) thin films in the temperature range of 213-290\textdegree K. They reported that the conduction in the temperature range 213-296\textdegree K takes place through hopping in the localized state near Fermi level while in the temperature range from 296-390 \textdegree K, conduction takes place due to thermally assisted tunneling of electrons in the localized state. M. Ahmad et al. [104] investigated the electrical properties of Sn\textsubscript{10}Sb\textsubscript{20-x}Bi\textsubscript{x}Se\textsubscript{70} (x = 0, 2, 4, 6 and 8) thin films. They reported that the value of pre-exponential factor (σ\textsubscript{0}) indicates that the conduction is due to extended and localized states as well. D. Singh et al. [105] reported the electrical properties of (Se\textsubscript{80}Te\textsubscript{20})\textsubscript{100-x}
Ag ultra thin films. Thin films were annealed in the temperature range $328-343^\circ$K. The dc activation energy decreases with increasing Ag concentration.

1.5 Applications of Chalcogenide Glasses

Chalcogenides glasses provide a versatile platform for various structural, thermal, optical and electrical applications. Chalcogenide glasses can be formed with a wide range of compositions and doped with additional elements from Group III to VI to enhance its functionality. Chalcogenide glasses have potential applications in xerography, optical memory devices, remote sensing, optical limiting, optical biosensors and optical limiting etc. Optical limiting is used in defense to protect detectors from laser fire because intensity blasts from infrared lasers can destroy the sensitive detectors used for surveillance [106]. These devices can be protected against pulses of high intensity laser by placing a non-linear optical material in front of the detector. Such a material must be transparent to low intensity infrared light. Optical non-linear materials of higher refractive index are suitable for optical limiting [107]. The chalcogenide glasses possess large non-linear optical characteristics and exhibit transparency in IR region having wavelength 1-12 μm. They are important for infrared imaging and remote sensing. Since impurities added to chalcogenide glasses reduce the transparency of glasses, therefore they can be controlled by preparation and purification methods.

Optical fibers containing chalcogenide glasses have remarkable properties such as structural, optical and thermal etc and therefore they play an important role in the development of optical biosensors [108]. They are used in fabrication of core-cladding structure. Due to wide optical window in infra red region, chalcogenides glasses are promising candidates for sensing the fingerprint region of bio-molecules including carbohydrates, nucleic acids, proteins and lipids etc [109]. Fabrication of memory and
threshold devices depends upon the tendency of material to crystallize. Memory switches come from the boundaries of glass forming regions where glasses are more prone to crystallization. The glasses that can be easily devitrified undergo phase change and hence are useful for memory devices [110]. The tendency of glasses to crystallize depends on the difference of glass transition temperature \((T_g)\) and crystallization temperature \((T_c)\). The glasses having small difference \((T_c-T_g)\) are stable and can be used in memory devices. Chalcogenide glasses have these properties and hence can be used as data storage devices.

1.6 Objective of Study

Chalcogenide glasses in bulk form and thin films exhibit a wide variety of changes in their structural, thermal, optical and electrical properties. The electrical transport properties and is explored through several interrelated analytical investigations. Davis-Mott model has been used to describe the electrical transport properties. Among chalcogenides glasses, Se is characterized with high viscosity and hence, has good glass forming ability. This makes Se a good host matrix for investigation in bulk alloys and thin films as well. However, pure Se has some disadvantages such as short lifetime, less robust and low sensitivity. This problem can be overcome by alloying Se with other some other elements from Group III-VI such as In, Bi, Sb and Pb etc.

A lot of research has been carried out on chalcogenide glasses for the development of new advance materials for future aspects. Most of the application of these materials depends on the ability to engineer the materials composition to meet the specific requirement of the system. In order to meet this requirement, it is necessary to develop low cost methods for preparing the chalcogenide glasses. It is the properties of a material that eventually determine its usefulness in an application. The series of the materials prepared in this thesis have applications in solid state devices, memory devices and
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opto-electronic devices etc based on their structural, thermal, optical and electrical properties. The structural property and the characterization of materials are covered within the series to develop new materials which have always been fundamentally and intrinsically important to material science and engineering. Chalcogenide glasses make its unique space for basic science and technological application and engineers working in solid state physics devices like photovoltaic devices, sensor, memory switching and optical recording. A research in this field is strongly motivated by the need of scientific industry. They are the most favorable materials having excellent structural, thermal, optical, and electrical properties, which can be used for different technical approach and modern industry.

The present study is a systematic investigation of structural, thermal, optical and electrical properties of ternary and quaternary chalcogenide glasses. Thin films were prepared by thermal evaporation technique. Structural properties of bulk alloys and thin films were studied using X-Ray diffraction (XRD), glass morphology by Scanning electron microscope (SEM) and elemental composition by Energy dispersive x-ray spectroscopy (EDS) Particular emphases are given on ternary and quaternary chalcogenide glasses. Thermal analysis such as transition temperature, enthalpy and activation energy have been carried out using DSC. Optical parameters have been determined in the ultra violet – visible range of wavelength from 190-100 nm using UV-Vis Spectrophotometry. DC conductivity has been investigated by two prob methods using sample holder. Chalcogenide glasses have a large density of defect states because of absence of long range order, which introduce a large localized state in the chalcogenide glasses.

In this thesis, the following work has been carried out:

- Structural and Thermal Study of $\text{In}_x\text{Se}_{96-x}\text{S}_x$ ($x = 0, 4, 8, 12$) Bulk Alloys
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- Structural and Thermal Study of $\text{In}_3\text{Te}_7\text{Bi}_x\text{Se}_{90-x}$ ($x = 0, 5, 10$ and $15$) Bulk Alloys

- Structural, Optical and Electrical Study of $\text{In}_3\text{Te}_7\text{Bi}_x\text{Se}_{90-x}$ Thin Films

The entire work presented in this thesis is divided in seven chapters. Layout of thesis is as follows:

The basic overview of materials (crystalline and non-crystalline) has been discussed in Chapter - 1 entitled “Introduction”. In this chapter amorphous semiconductor, chalcogenide glasses and its properties such as structural, thermal, optical and electrical have been discussed. This also includes literature survey.

Chapter-2 deals with “Theoretical background”. In these chapters different band models such as Cohen, Fritzche and Ovshinsky (CFO) Model, Davis and Mott Model and Mott, Davis and Street (MDS) Model for conduction in amorphous semiconductors have been discussed. Defects in amorphous semiconductors have also been discussed. For thermal analysis, JMA model, Kissinger and Ozawa equation for determination of activation energy of crystallization have been used. Structural relaxation or activation energy for glass transition has been determined using Moynihan et al equation. Method of determination of optical and electrical parameters has been discussed.

Chapter-3 entitled “Experimental Techniques” deals with the different experimental techniques and preparation of bulk glassy alloys and thin films. X-ray Diffraction (XRD) analysis, Energy Dispersive Analysis by X-ray (EDX) and Scanning Electron Microscope (SEM) of the bulk alloys and thin films has been discussed. For study of thermal properties of $\text{In}_4\text{Se}_{96-x}\text{S}_x$ ($x=0, 4, 8, 12$) and $\text{In}_3\text{Te}_7\text{Bi}_x\text{Se}_{90-x}$ ($x = 0, 5, 10, 15$) bulk alloys, Differential Scanning Calorimetry (DSC) and Differential Thermal Gravimetric (TGA) were carried out. Ultraviolet-Visible Spectroscopy (UV-Vis) of
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In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10, 15) thin films carried out to determine the optical parameters. Electrical parameters were measured using DC two probe methods.

Chapter-4 presents the study of structural analysis In$_4$Se$_{96-x}$S$_x$ (x = 0, 4, 8, 12) chalcogenide bulk glasses using XRD, SEM and EDS and determination of thermal properties such as transition temperature, activation energy and enthalpy of bulk alloys using Kissinger, Ozawa and Moynihan et al equations applying JMA model.

Chapter-5 deals with structural and thermal properties of quaternary chalcogenide glasses In$_3$Te$_7$Bi$_x$Se$_{90-x}$ (x = 0, 5, 10 and 15) bulk alloys. Structural properties of the alloys were studied by XRD, SEM and EDX and thermal analysis was carried out using DSC.

Chapter-6 describes the structural, optical and thermal study of In$_3$Te$_7$Bi$_x$Se$_{90-x}$ thin films. Structural analysis of thin films was carried out by XRD, SEM and EDS. Optical parameters optical band gap ($E_g$), extinction coefficient (k), refractive index (n), dielectric constant and loss ($\varepsilon '_r$, $\varepsilon ''_r$) were determined. Electrical parameters such as DC conductivity ($\sigma _d$), pre-exponential factor ($\sigma _0$), activation energy ($\Delta E$) and carrier density ($n_c$) have been measured.

Chapter-7 summarizes the conclusion and future prospectus of whole thesis.


Chapter 1


Chapter 1


Chapter 1


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[110] Al-Agol, F. A. "Crystallization kinetics and effect of thermal annealing on optical constants in a-Ge25Se75− xTex glasses." 