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Crystallization Kinetics of Chalcogenide Glasses

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1. Introduction

1.1 Background of chalcogenides

Chalcogenide glasses are disordered non crystalline materials which have pronounced tendency their atoms to link together to form link chain. Chalcogenide glasses can be obtained by mixing the chalcogen elements, viz, S, Se and Te with elements of the periodic table such as Ga, In, Si, Ge, Sn, As, Sb and Bi, Ag, Cd, Zn etc. In these glasses, short-range inter-atomic forces are predominantly covalent: strong in magnitude and highly directional, whereas weak van der Waals' forces contribute significantly to the medium-range order. The atomic bonding structure is, in general more rigid than that of organic polymers and more flexible than that of oxide glasses. Accordingly, the glass-transition temperatures and elastic properties lay in between those of these materials. Some metallic element containing chalcogenide glasses behave as (super) ionic conductors. These glasses also behave as semiconductors or, more strictly, they are a kind of amorphous semi-conductors with band gap energies of $1\pm 3\text{eV}$ (Fritzsche, 1971). Commonly, chalcogenide glasses have much lower mechanical strength and thermal stability as compared to existing oxide glasses, but they have higher thermal expansion, refractive index, larger range of infrared transparency and higher order of optical non-linearity.

It is difficult to define with accuracy when mankind first fabricated its own glass but sources demonstrate that it discovered 10,000 years back in time. It is also difficult to point in time, when the field of chalcogenide glasses started. The vast majority of time the vitreous glassy state was limited to oxygen compounds and their derivatives. Schulz-Sellack was the first to report data on oxygen-free glass in 1870 (Sellack, 1870). Investigation of chalcogenide glasses as optoelectronics materials in infra-red systems began with the rediscovery of arsenic trisulfide glass (Frerichs, 1950, 1953) when R. Frerichs was reported his work. Development of the glasses as a practical optoelectronic materials were continued by W. A. Fraser and J. Jerger in 1953 (Fraser et. al., 1953). During the 1950-1970 periods (Hilton, 2010) the glasses were made in ton quantities by several companies and it frequently used in commercial devices. As an example, devices were made to detect the overheated bearings in the railroad cars. Hot objects could be detected by the radiation transmitted through the 3- to 5 μm atmospheric window, for this transparent arsenic trisulfide glass was used. While, to make chalcogenide glass compositions which capable in transmitting longer wavelengths arose the concept of passive thermal optical systems was adopted.

Jerger, Billian, and Sherwood (Hilton, 1966 & 2010) extended their investigation on arsenic glasses containing selenium and tellurium and later adding germanium as a third constituent. The goal was to use chalcogen elements heavier than sulfur to extend long-wavelength transmission to cover the 8- to 12 μm window with improved physical properties. A subsequent work also in Ioffe Institute, in Lenin-grad under the direction of Boris Kolomiets was also reported in 1959 (Hilton, 2010). Work along the same line was begun in the United Kingdom by Nielsen and Savage (Nielsen, 1962, Savage et. al., 1964, Savage et. al., 1966) as well as work also at Texas Instruments (TI) began as an outgrowth of the thermoelectric materials program. The glass forming region for the silicon-arsenic-tellurium system was planned by Hilton and Brau (Hilton et. al., 1963). This development led to an exploratory DARPA- ONR program from 1962 to 1965 (Hilton, 2010). 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. Further, Hilton (Hilton, 1974) also worked on sulfur-based glasses in 1973 to 1974. The exploratory programs resulted in eight chalcogenide glass U.S. patents and a number of research papers published in an international journal detailing the results (Hilton et. al., 1966). After that scientific community made serious effort in development of chalcogenide glasses and organized symposia and meetings in All-Union Symposium on the Vitreous Chalcogenide Semiconductors held in May 1967 (Kokorina, 1966) in Leningrad (now called St. Petersburg). In that symposium Stanley Ovshinsky (founder of Electron Energy Conversion Devices in Troy, Michigan) was presented his first paper dealing with switching devices based on the electronic properties of chalcogenide glasses. Similar work was reported by A. D. Pearson (Pearson, 1962) in United States, thus started a great world wide effort to investigate chalcogenide glasses and their electronic properties. The purpose was to pursue a new family of inexpensive electronic devices based on amorphous semiconductors. The effort in this field far exceeded the effort directed toward optoelectronics applications. Some of the results of the efforts in the United States were reported in a symposium (Doremus, 1969) and in another symposium (Cohen et. al., 1971). In this order Robert Patterson mapped out the glass forming region for the germanium-antimony-selenium system and granted a U.S. patent (Patterson, 1966-67) covering the best composition selection.

In 1967 Harold Hafner was made many important contributions including a glass casting process and a glass tempering process in Semiconductor Production Division under the direction of Charlie Jones. Their work concentrated the efforts on a glass from the germanium-arsenic-selenium system and outcomes (Jones et. al., 1968) agreed with the conclusions of the Russian, U.K. Alternatively, Servo group efforts that the germanium-arsenic-selenium system produced the best glasses for infrared system applications. Don Weirauch (Hilton, 2010) was conducted a crystallization study on the germanium-arsenic selenium family of glasses and identified a composition in which crystallites would not form. In 1972 a commercial group was successfully cast (12 in 24 in 0.5 in) a window which flat polished, parallel and antireflection-coated (Hafner, 1972). In the late 1960s and early 1970s, passive 8- to 12 μm systems began to be produced in small numbers mostly for the defense uses.

In 1968, Ovshinsky and his co-workers were discovered (Stocker, 1969) that some chalcogenide glasses exhibited memory and switching effects. After this discovery it became clear that the electric pulses could be used to switch the phases in chalcogenide glasses back and forth between amorphous and crystalline state. Around the same period in 1970's, Sir N. F. Mott (a former Nobel Prize winner in Physics-1977) and E.A. Davis were developing the

theory on the electronic processes in non-crystalline chalcogenide glasses (Mott et. al., 1979), and Kawamura (Kawamura et. al., 1983) was discovered xerography. Applications of solar cells were developed by Ciureanu and Middehoek (Ciureanu et. al., 1992) and Robert and his coworkers (Robert et.al., 1998). Infrared optics applications were studied by Quiroga and Leng and their coworkers (Quiroga et al., 1996, Leng et. al., 2000). The switching device applications were introduced by Bicerono and Ovshinsky (Bicerono et. al.,1985) and Ovshinsky (Ovshinsky, 1994). P. Boolchand and his coworkers (Boolchand et.al., 2001) was discovered intermediate phase in chalcogenide glasses. In this order several investigators have been also reported that the useful optoelectronics applications in infrared transmission and detection, threshold and memory switching (Selvaraju et al., 2003), optical fibers (Bowden et al., 2009, Shportko et al., 2008, Milliron et al.,2007) functional elements in integrated-optic circuits (Pelusi et al.2009) non-linear optics (Dudley et al., 2009), holographic & memory storage media (Vassilev et al., 2009, Wuttig et al.,2007), chemical and bio-sensors (Anne et al.,2009, Schubert et at., 2001), infrared photovoltaics (Sargent, 2009), microsphere laser (Elliott, 2010), active plasmonics (Samson,2010), microlenses in inkjet printing (Sanchez, 2011) and other photonics (Eggleton, 2011) applications. In this respect, the analysis of the composition dependence of their thermal properties was an important aspect for the study (Singh et al., 2009, 2010, 2011).

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 1983. However, first book entirely dedicated to chalcogenide glassy materials entitled "Chalcogenide Semiconducting Glasses" was published in 1983 by Z.U.Borisova. In this order, G.Z. Vinogradova was published her monograph "Glass formation and Phase Equilibrium in Chalcogenide Systems" in 1984. M.A. Andriesh dedicates a book to some specific applications of chalcogenide glasses entitled "Glassy Semiconductors in Photo-electric Systems for Optical Recording of Information". M.A. Popescu gave large and detailed account on physical and technological aspect of chalcogenide systems in his book "Non-Crystalline Chalcogenides". The compendium of monographs on the subject of photo-induced processes in chalcogenide glasses entitled "Photo-induced Metastability in Amorphous Semiconductors" was compiled by A. Colobov-2003. Robert Fairman and Boris Ushkov-2004 described physical properties in "Semiconducting Chalcogenide Glass I: Glass formation, structure, and simulated transformations in Chalcogenide Glass". Finally, A. Zakery and S.R. Elliott demonstrated the "Optical Nonlinearities in Chalcogenide Glasses and their Applications" in 2007.

1.1.1 Binary chalcogenides

Structure of chalcogenide glasses have been extensively studied in binary compositions considering both the bulk and thin film forms. Chalcogens can form alloys together, Se-S, Se-Te (Gill, 1973) and S-Te amorphous (Sarrach et. al, 1976, Hawes, 1963) compounds were identified; however the scientific community seems to have, for the moment at least, left these glasses aside. Many binary compounds can be synthesized by associating one of the chalcogen with another element of the periodic table like, indium, antimony, copper, germanium, phosphorus, silicon and tin. A few other compounds based on heavy or light elements and alkali atoms have also been investigated. Abrikosov and his co-workers in 1969 (Lopez, 2004) were first reported the molecular structures of most extensively studied As-S, As-Se binary chalcogenide alloys in their monograph, the phase diagrams for the As- S

and As-Se systems. As-S alloys can be formed with an As content up to 46%, while in As-Se this maximum content can be raised to almost 60%. Glasses with low As content can easily crystallize (e.g. for a content of 6% As the glass crystallizes at room temperature in one day) in the range 5-16 weight %, in a couple of days at 60°C while it takes 30 days for As S at 280°C (Lopez, 2004). As-Se alloys can crystallize along the all composition range, however this was to be done under pressure and at elevated temperatures. The typical As_2S_3 structure has usually pictured as an assembly of six AsS pyramids (the As atom being the top of the pyramid while three S atoms form the base). Goriunova and Kolomiets in 1958 (Lopez, 2004) were pointed out that the importance of covalent bonding in chalcogenide glasses as the most important property to make stability of these glasses. As opposed to metallic bonding, covalent bonding ensures easier preparation of the glasses. Thus, the crosslinking initiated by the As atoms should reduce the freedom for disorder in which bonds are covalent. Further Vaipolin and Porai-Koshits reported X-ray studies in beginning of the 1960's (Lopez, 2004), for the vitreous As_2S_3 and As_2Se_3 and a number of binary glass compositions based on these two compounds. These glasses were shown to contain corrugated layers, which deformed with increasing size of the chalcogens and arsenic atoms became octohedrally coordinated. The character of the bonds was also found become more ionic when at equimolecular compositions. At the beginning of the 1980's, Tanaka was also characterized the chalcogenide glasses as a phase change materials and demonstrated that they structurally rigid and not having long-range ordering.

Alternatively, Se-S, Se-Te and S-Te (Hamada et. al., 1968, Bohmer & Angell, 1993) were extensively studied binary chalcogens alloys in which Se and S taken as host material. Amorphous selenium and sulfur molecular structure become the mixture of chain and rings which bridging the gap between molecular glasses and polymers. They covalently bonded with two coordination number. The most stable trigonal structural phase α -Se consists of parallel helical chains and two monoclinic bonds forms the composed of rings of eight atoms. These polymorphs distinguished by the correlation between neighboring dihedral angles. The amorphous selenium has relatively low molecular weight polymer with low concentration of rings (Bichara & pellegatti, 1993, Caprion & Schober, 2000 & 2002, Echeveria et. al., 2003, Malek et. al., 2009, etc).

Particularly Se-In binary chalcogenide compositions were getting much attention due to their versatile technical applications. VI- III family compounds Se- In form layered structures with strong covalent bonds. Basically VI-III group Se- In compounds have hexagonal symmetry structure. It consists of two layers which separated by tetrahedrally or pentagonally coordinated Se and In (JablÇonska et. al., 2001 & Pena et al., 2004). Amorphous Se-In compounds contains α - In_2Se_3 , α -InSe, and α - In_4Se_3 binary phases. The number of In-Se nearest neighbor heteropolar bonds considerably larger than the homopolar bonds. The In-In and Se-Se homopolar bonds contribute mainly to the left- and right-hand side of the first peak in the radial distribution function, but they do not influence original position. The number of nearest-neighbor Se-Se bonds in α -InSe and α - In_4Se_3 structures is generally negligible (Kohary et. al., 2005).

1.1.2 Ternary chalcogenides

Ternary chalcogenide glasses also broadly studied from more than three decades. Ternary chalcogenides can be prepared by introducing a suitable additive element in well known or

new binary matrix. Most extensively studied ternary As-S-Se system was shown a very wide glass-forming region (Flaschen et. al., 1959). The solid solutions can be formed along the line $As_2 S_3 - As_2 Se_3$ which proved via IR spectra and X-ray analysis by Velinov and his coworkers (Velinov et. al., 1997). The Covalent Random Network (CRN) and the Chemically Ordered Network (CON) models both satisfy the 8-N rule under the distribution of bond types in a covalent network with multi elements. As- rich glasses can be formed As-As, As-Se, and As-S bonds; thus Se-rich glasses have As-Se, As-S, and Se-Se bonds and S-rich glasses As-Se, As-S, and S-S bonds. The relative weight of each of the above units is expected to be proportionate to the overall composition of the glass itself (Yang et. al., 1989).

In recent years Zn containing ternary chalcogenide glasses attracted much attention due to higher melting point, metallic nature and advanced scientific interest (Boo et. al., 2007). Crystalline state zinc has hexagonal close-packed crystal structure with average coordination number four. While, in amorphous structure it is expected to metallic Zn dissolve in Se chains and makes homopolar and heteropolar bonds. Addition of third element concentration in binary alloy affects the chemical equilibrium of exiting bonds, therefore newly form ternary glass stoichiometry would heavily cross-linked, and makes homopolar and heteropolar bonds in respect of alloying elements. Specifically, Se-Zn-In ternary chalcogenide glasses can form Se-In heteronuclear bonds with strong fixed metallic Zn-In, Zn-Se bonds. Incorporation of indium concentration as-cost of selenium amount, the Se-Zn-In became heavily cross-linked results the steric hindrance increases at the threshold compositional concentration and beyond the threshold concentration a drastic change in physical properties has been observed.

1.1.3 Multicomponent chalcogenides

Addition of more than three elements in chalcogenide alloys refers as multicomponent alloys. In recent years there is an intensive interest made on study of new multi-component chalcogenide glasses to make sophisticated device technology as well as from the point of view of basic physics. Although Se rich binary and ternary chalcogenide glasses exhibit high resistivity, greater hardness, lower aging effect, enhanced electrical and optical properties with good working performance. But ternary glasses have certain drawbacks which implying the limitation in applications. It is worth then to add more than two components into selenium matrix can produce considerable changes in the properties complex glasses. Predominantly, metal and semimetal containing multi-component amorphous semiconductors promising materials to investigations such as; Ge-Bi-Se-Te, Al-(Ge-Se-Y), Ge-As-Se-Te, Cd (Zn)- Ge(As), $GeSe_2 - Sb_2Se_3 - PbSe$, $Cu_2ZnSnSe_4$ etc. (Thingamajig et. al., 2000, Petkov, 2002, Vassilev, 2006, Wibowo et. al. 2007). More specifically Se-Zn-Te-In multi-component chalcogenide glasses make Se-In heteronuclear bonds with other possible bonds Zn-In and Te-In. Due to the addition of Indium in quaternary glassy matrix, the structures become heavily cross-linked and steric hindrance increases. Therefore, at the expanse of Se chains and replacement of weak Se-Se bonds by Se-In bonds results the increase and decrease in their associative physical properties of Se-Zn-Te-In glasses.

Therefore, the thermal, electrical and optical properties of chalcogenide glasses widely depend on alloying concentration and intrinsic structural changes make them a chemical threshold a particular concentration of alloy. In view of these basic property several past research work in chalcogenide glasses were reported on binary, ternary and very few on

multicomponent systems (Tonchev et. al., 1999, Wagner et. al., 1998, Mehta et. al., 2008, Patial et. al., 2011, Malek et. al., 2003, Soltan et. al., 2003, Song et. al., 1997, Usuki et. al., 2001, Fayek et. al., 2001, Wang et. al., 2007, Vassilev et. al., 2007, Eggleton et. al., 2011, Prashanth, et. al., 2008, Vassilev et. al., 2007, Othman et. al., 2006, Zhang et. al., 2004, Hegab et. al., 2007, Narayanan et. al., 2001, etc). Scientific and technological drawbacks, like low thermal stability, low crystallization temperature and aging effects (Guo et. al., 2007, Boycheva et. al., 2002, Ivanova et. al., 2003, Vassilev et. al., 2005, Xu et. al., 2008, Troles et. al., 2008) of non-metallic binary and ternary alloys motivates to investigators to make metallic multicomponent chalcogen alloys to achieve high thermal stability and harder chalcogenide glasses (Pungor, 1997, Demarco et. al., 1999, Kobelke et. al., 1999, Zhang et. al., 2005, Singh, 2011).

Extensive research on metal containing multicomponent chalcogenide alloys was begin nearly end of nineties when Kikineshy and Sterr 1989 & 1990 (Kokenyesi, et. al., 2007 & Ivan & Kikineshi, 2002) were demonstrated the multilayer of chalcogen alloys simply nanostructures materials which can be rather easily produced with controlled geometrical parameters. In this order Ionov and his coworkers (Ionov et. al., 1991) were demonstrated the electrical and electrophotographic properties of selenium based metal containing multicomponent chalcogenide glass and outlined these materials would be useful for electrophotographic and laser printer photoreceptors. Saleh and his coworkers (Saleh et. al., 1993) were studied the nuclear magnetic resonance relaxation of Cu containing chalcogenide glasses. Carthy & Kanatzidis (Carthy & Kanatzidis, 1996) were introduced the bismuth and antimony containing new class of multicomponent chalcogenide glasses. In the same year Natale and his coworkers (Natale et. al., 1996) were demonstrated the heavy metal multicomponent glasses useful for array sensors. Further, Nesheva and his coworkers (Nesheva et. al., 1997) were studied the amorphous pure and alloying selenium based multilayers and demonstrated the photoreceptor properties at room temperature unaltered throughout in a year. Efimov (Efimov, 1999) was described the mechanism of formation of the vibrational spectra of glasses such as quasi-molecular model, central force model and its recent refinements (model of phonon localization regions) and deduce the trends in the IR and Raman band assignments in inorganic systems. Goetzberger & Hebling (Goetzberger & Hebling, 2000) were commented on the present, past and future of photovoltaic materials. In the same year Naumis (Naumis, 2000) demonstrated the jump of the heat capacity in chalcogenide glasses during glass transition and show change in glass fragility and excess thermal expansivity is a function of average coordination number. While Mortensen and his coworkers (Mortensen et. al., 2000) were used heavy metals based chalcogenides sensors in detection of flow injection. Mourizina and his coworkers (Mourizina et. al., 2001) were demonstrated the ion selective light addressable potentiometric sensor based on metal containing chalcogenide glass film. In the same year Rau and his coworkers (Rau et. al., 2001) were studied the effect of the mixed cation in chalcogenide glasses and reported that the non-linear structural changes in Raman and infrared spectra. Further, Messaddeq and his coworkers (Messaddeq et. al., 2001) were demonstrated the light induced volume expansion in chalcogenide glasses under the irradiation UV light. Moreover, Hsu and Narayanan and their coworkers (Hsu et. al., 2001, Narayanan et. al., 2001) were studied the near field microscopic properties of electronic & photonic materials and devices and large switching fields in metal containing chalcogenide glasses owing to chemical disordering. Salmon & Xin (Salmon & Xin, 2002) were studied the effect of high modifier content

corresponding to coordination number and demonstrate the structural motifs change in such materials. Subsequently, Agarwal & Sanghera (Agarwal & Sanghera, 2002) were discussed the development and application of chalcogenide glass optical fibers in near scanning field microscopy/spectroscopy and Jackson & Srinivas (Jackson & Srinivas, 2002) demonstrated the modeling of metallic chalcogenide glasses using density function theory calculations. Tanaka (Tanaka, 2003) reviewed the nanoscale structures of chalcogenide glasses and inspect surface modifications at nanometer resolution and Micoulaut & Phillips (Micoulaut & Phillips, 2003) were shown the three elastic phases of covalent networks (I) floppy, (II) isostatically rigid, and (III) stressed-rigid) depend on the degree freedom of material. They were also suggested that the ring factor is responsible for high crystallization temperature in metallic/ semi-metallic chalcogenide glasses. Lezal and his coworkers (Lezal et. al., 2004) were reviewed the chalcogenide glasses for optical and photonics applications. Vassilev & Boycheva (Vassilev & Boycheva, 2005) were critically reviewed the achievements in application of chalcogenide glasses as membrane materials. They were also demonstrated that the advantages and disadvantages in analytical performance and compared with the corresponding polycrystalline analogous. Emin (Emin, 2006) was explained the polaron conduction machines in amorphous semiconductors and Kokenyesi (Kokenyesi, 2006) reviewed the amorphous chalcogenide nano-multilayers: research and developments. While Phillips (Phillips, 2006) demonstrated the, ideally glassy materials have hydrogen-bonded networks. Bosch and his coworkers (Bosch et. al. 2007) were critically reviewed the last decade developments in optical fibers in bio sensing and Vassilev and his coworkers (Vassilev et. al., 2007) introduced the new Se- based multicomponent chalcogenide glasses and studied their composition dependence physical properties. Furthermore, Wachter and Taaed their coworkers (Wachter et. al., 2007, Taaed et. al., 2007) were demonstrated the composition dependence reversible and tunable glass-crystal-glass phase transition properties in new class of multicomponent chalcogenide glasses and show chalcogenide glasses useful for all-optical signal processing devices due to their large ultrafast third-order nonlinearities, low two-photon absorption and the absence of free carrier absorption in a photosensitive medium. Dahshan and Lousteau and their coworkers (Dahshan et. al., 2008, Lousteau et. al., 2008) were demonstrated the thermal stability and activation energy of some Cu doped chalcogenide glasses and the fabrication of heavy metal fluoride glass to explore the optical planar waveguides by hot-spin casting. Further, Klokishner (Klokishner et. al., 2008) were studied the concentration effects on the photoluminescence band centers in multicomponent metallic chalcogenide glasses and Ielmini and his coworkers (Ielmini et. al., 2008) demonstrated the threshold switching mechanism by high-field energy gain in the hopping transport of chalcogenide glasses. Mehta and his coworkers (Mehta et. al., 2009) were studied the effect of metallic and non metallic additive elements on Se-Te based chalcogenide glasses. In the same year Turek and Anne their coworkers (Turek et. al., 2009, Anne et. al., 2009) were demonstrated the artificial intelligence/fuzzy logic method for analysis of combined signals from heavy metal chemical sensors and commented on, due to the remarkable properties of chalcogenide glasses can be used as a biosensor which can collect the information on whole metabolism alterations rapidly. Further, Khan and his coworkers (Khan et. al., 2009) were demonstrated the composition dependence electrical transport and optical properties of metallic element doped Se based chalcogenide glasses. In order to this Snopatin and his coworkers (Snopatin et. al., 2009) were demonstrated the

some high purity multicomponent chalcogenide glasses for fiber optics. Kumar and his coworkers (Kumar et. al., 2010) were demonstrated the calorimetric studies of Se-based metal containing multicomponent chalcogenide glasses. Peng & Liu (Peng & Liu ,2010) were reviewed the advances and achievements in SPM-based data storage in viewpoint of recording techniques including electrical bistability, photoelectrochemical conversion, field-induced charge storage, atomic manipulation or deposition, local oxidation, magneto-optical or magnetic recording, thermally induced physical deformation or phase change, and so forth as well as achievements in design and synthesis of organic charge-transfer (CT) complexes towards thermochemical-hole-burning memory, the correlation between hole-burning performances and physicochemical properties of CT complexes.

Story of the investigations will be remain continue in field of metallic chalcogenides (not limited to above outlined the major events) to deduce the new future prospective multicomponent chalcogenide glassy alloys. Amorphous chalcogenide alloys which full fill the essential requirement of modern optoelectronics. So, it can be outlined potential field of optoelectronics and advanced material is rapidly growing owing to their possible uses. Therefore, it is important to have an understanding regarding on crystallization process of chalcogenide glasses (predominately in metal containing alloys).

1.2 Crystallization

Crystallization is a natural process of formation of solid crystals from a solution/- melt. Crystallization of a substance can also achieve from the chemical solid-liquid separation technique, in which mass transfer from the liquid solution to a pure solid crystalline phase. The crystallization process of a substance mainly consists of two major events nucleation and crystal growth. In nucleation process the molten molecules dispersed in solid solution and begin to formation of clusters at the nanometer scale. Crystal growth is the subsequent growth of the nuclei which develop critical size of the formed clusters (because size of clusters plays an important role in the application of the material). Hence, the nucleation and growth are the continuous process which occurs simultaneously when supercooling exists in a system. Thus, system supercooling state acts as a driving force for the crystallization process. The supercooling driving force depending upon the conditions, either nucleation or growth may be predominant over to other and outcomes can be formed crystals with different sizes and shapes. Once the supercooling is established in a solid-liquid system and reached at equilibrium then crystallization process is completed (Mersmann, 2001).

In general supercooled materials/ or alloys have ability to crystallize with different crystal structures, this process is known as polymorphism. Each polymorph is in fact a different thermodynamic solid state and crystal polymorphs of the same alloy/-compound which exhibited different physical properties, such as dissolution rate, shape, melting point, etc. Thus the crystallization process of a substance is governed by both thermodynamic and kinetic factors which highly variable and difficult to control. Factors those affect the crystallization process of a substance/alloy are the impurity level, mixing regime, vessel design, and cooling profile and shape of crystals. Usually in those materials crystallization process occurs at lower temperatures, in supercooling situation they obey the law of thermodynamics. Its literal meaning a crystal can be more easily destroyed than it is formed.

Subsequently it is easier to a perfect crystal in a molten solid than to grow again a good crystal from the resulting solution. Hence the nucleation and growth process of a crystal are well control under the thermodynamic kinetic.

1.3 Nucleation and growth

1.3.1 Nucleation

Nucleation of the substance reflects the initiation of a phase change in a small region cause the formation of a solid crystal from a liquid solution. It is a consequence of rapid local fluctuations on a molecular scale in a homogeneous phase which define as a metastable equilibrium state. The whole nucleation process of a substance is the sum of heterogeneous (nucleation that occurs in the absence of a second phase) and heterogeneous (nucleation that occurs in the presence of a second, foreign phase) category of nucleation. Homogeneous nucleation due to clustering of molecules (embryos) in a supersaturated environment, in which a process began, combines two or more than molecules. In the reversible clustering process a few molecules grew at the same time and others dissolving. Once embryos attained a certain critical size then it decrease its total free energy by growing and becomes stable (Reid et. al., 1970). But, in practice it is difficult to find complete homogeneous nucleation owing to presence of insoluble amounts of matter even in pure material. Therefore, heterogeneous nucleation is always associated with homogeneous nucleation due to presence of second phase in bulk molten material. The heterogeneous nucleation occurs in a random fashion at various sites in a matter.

1.3.2 Crystal growth

As earlier mentioned crystal growth is the successive process of nucleation in which the critical nuclei of microscopic size form a crystal. Crystal growth in crystallization process takes place by fusion and re-solidification of the material. In this process within a solid material constituent of molecules (embryos) are arranged in an orderly repeating pattern extending in all three spatial dimensions. Crystal growth is a major stage of a crystallization process which consists the addition of new molecules (embryos) strings into the characteristic arrangement of a crystalline lattice. The growth typically follows an initial stage of either homogeneous or heterogeneous nucleation. The crystal growth process yields a crystalline solid whose molecules are typically close packed with fixed positions in space relative to each other. In general crystalline solids are typically formed by cooling and solidification from the molten (or liquid) state. As per the Ehrenfest classification it is first-order phase transitions with a discontinuous change in volume (and thus a discontinuity in the slope or first derivative with respect to temperature, dV/dT) at the melting point. Hence, the crystal and melt are distinct phases with an interfacial discontinuity having a surface of tension with a positive surface energy. Thus, a metastable parent phase represents it always stable with respect to the nucleation of small embryos from a daughter phase with a positive surface of tension. Hence, crystal growth process is first-order transitions consist advancement of an interfacial region whose structure and properties vary discontinuously from the parent phase. In the crystal growth process stiochiometry of glass compositions do not undergo in compositional changes during crystallization, mean, no need to long-range diffusion (Swanson, 1977) for crystal growth in chalcogenide glasses; thus, interfacial rearrangements are likely to control the crystal growth process. This (melt quenched) type of

crystal growth is generally described from these three basic standard models: (i) the screw dislocation model; (ii) the normal or continuous growth model; and (iii) the two-dimensional surface nucleation growth.

Theoretically, nucleation and crystal growth process of molten solids first reported by Volmer and Weber (Volmer and Weber, 1925) and later on it explained in a large amount of literature. Tammann (1925) discussed the theory of nucleation and crystal growth and outlined the various parameters involved in terms of a probabilistic model involving a functional relation to pressure, temperature, and time. Many later studies deal with the nucleation and growth of crystals on an atomistic level. Nucleation of crystals from a melt is the mobility of atoms and molecules in the melt as measured by the diffusion coefficient. In glass-forming systems, liquid diffusion coefficients drop markedly with decreasing temperature (Towers and Chipman, 1957). When temperature drops below the liquidus, nucleation will increase from zero to a maximum at some undercooling. Diffusion rates then very low and nucleation decreases with further decrease in temperature. This explains the pattern of nucleation in liquids where the liquid diffusivity decreases with temperature and finally it grow a crystal. Rate of growth is thus a function of mobility of crystal-forming species within the melt. Mobility, can be measured by the diffusion coefficient, as drops with decreasing temperature and growth rate, like nucleation.

Thermodynamics of crystal growth process in molten solids can be expressed as (Warghese, 2010); the thermodynamical equilibrium between solid and liquid phases occur when the free energy of the two phases are equal

$$G_L = G_S \quad (1)$$

here G_L and G_S are representing solid and liquid phases free energies

Free energy, internal energy and entropy of a system can be related from the Gibbs equation

$$G = H - TS \quad (2)$$

here G is the Gibbs free energy, H is the enthalpy, S is the entropy and T is the temperature.

Formation of a crystal can be considered as a controlled change of phase to the solid state. Therefore, the driving force for crystallization comes from the lowering of the free energy of the system during this phase transformation. Change in free energy in such transition can be related as;

$$\Delta G = \Delta H - T \Delta S \quad (3)$$

Where $\Delta H = H_L - H_S$

$$\Delta S = S_L - S_S$$

$$\Delta G = G_L - G_S$$

For the equilibrium $\Delta G = 0$

$$\Delta H = T_e \cdot \Delta S$$

Where, T_e is the equilibrium temperature

$$\Delta G = \Delta H \cdot \Delta T / T_e \quad (4)$$

Where $\Delta T = T_e - T$

ΔG is positive when $T_e > T$ and it depends on the latent heat of transition. The change in free energy can also represent as the product of change in entropy and super cooling temperature ΔT .

$$\Delta G = \Delta S \cdot \Delta T \quad (5)$$

Although equation (5) representing melt growth, in which one may depend on concentration rather than supercooling for solution growth and vapour growth. Equation (5) in more convent form can be expressed as;

$$\Delta G \sim RT \ln (C / C_0) \quad (6)$$

$$\Delta G \sim RT \ln (P / P_0) \quad (7)$$

In general form

$$\Delta G \sim RT \ln S \quad (8)$$

where R is the Rydberg constant, C , C_0 are the concentration of solid solution and concentration at critical transition, P , P_0 are the pressers in vapour phase and S is the supercooling ratio.

Thus the equations (4) and (6) explain how the free energy changes depend on the supercooling parameters which are decisive in the process of crystallization. The rate of growth of a crystal can be expressed as a monotonically increasing function of Gibbs free energy, when other parameters remain the same.

Since in nucleation process in the supercooled solution forms the small clusters of molecules (Joseph, 2010), therefore, free energy change between the solid and liquid can be expressed as ΔG_v and Gibbs equation can be written as;

$$\Delta G = 4\pi r^2 \sigma - 4/3 \pi r^3 \Delta G_v \quad (9)$$

where σ - is the interfacial energy and r is the spherical radius of the molecule

The surface energy increase in term of r^2 and volume energy decreases in term of r^3 . The critical size of nucleus can be obtained by the equation (9)

$$r^* = 2 \sigma / \Delta G_v \quad (10)$$

Hence the critical size (r^*) of the nucleus decreases with increasing cooling rate.

Further, in formation of critical nucleus size free energy (ΔG^*) change can be calculated as;

$$\Delta G^* = 16\pi\sigma^3 / 3\Delta G_v^2 \quad (11)$$

Equation (11) in terms of Gibbs thermodynamical relation can be written as;

$$\Delta G^* = 16\pi\sigma^3\Omega / 3(kT \ln.S)^2 \quad (12)$$

where Ω is the molecular volume

The rate of nucleation (J) can be expressed as;

$$J = J_0 \exp [-\Delta G^*/ kT] \quad (13)$$

or in terms of thermodynamical parameters

$$J = J_0 \exp [-16\pi\sigma^3\Omega^2/ 3k^3T^3 (\ln S)^2] \quad (14)$$

where J_0 is the pre-exponential factor

For critical supercooling condition $J = 1$, so that $\ln J = 0$, then expression can be expressed as;

$$S_{cri} = \exp [16\pi\sigma^3\Omega^2/ 3k^3T^3 \ln J_0]^{1/2} \quad (15)$$

1.4 Crystallization kinetics

Study of the crystallization of the amorphous materials with respect to time and temperature is called crystallization kinetics. Crystallization kinetic study of the materials can be performed in either isothermal or non-isothermal mode of Differential Scanning Calorimetry (DSC). In the isothermal method, the sample is brought near to the crystallization temperature very quickly and the physical quantities, which change drastically are measured as function of time. In the non-isothermal method the sample is heated at a fixed rate and physical parameters recorded as a function of temperature. Investigators (Sbirrazzuoli, 1999) preferred to perform DSC measurements in non-isothermal mode. Owing to fact, it is not possible to ensure the homogeneity (or constant) of DSC furnace temperature in isothermal mode during the injection of material sample.

Crystallization kinetics parameters of the materials generally interpreted at glass transition temperature (T_g), crystallization temperature (T_c) and peak crystallization temperature (T_p) with help well defined statistical approximations (such as Hurby, Ozawa, Augis and Bentt, Moynihan and Kissinger) (Hruby,1972, Ozawa, 1970, Augis & Bennett, 1978, Moynihan et al., 1974, Kissinger,1957). All the existing approximations described on the basis of JMA (Johnson,1939, Avrami, 1939& 1940) model statics, although in recent years investigators also reported the (Sanchez-Jimenez, 2009) JMA model not a universal model to explain the crystallization kinetics of the materials, because it has few limitations. Despite of this majority view of investigators toward to kinetic methods based on JMA model are more reliable to explain the crystallization of chalcogenide glasses, polymers, metallic and oxide glasses.

1.5 Theoretical basis of crystallization kinetics

In isothermal phase transformation the extent of crystallization (α) of a certain material can be represent from the Avrami's equation (Moynihan et al., 1974, Kissinger,1957, Johnson,1939)

$$\alpha(t)=1-\exp[(-Kt)^n] \quad (16)$$

where K is the crystallization rate constant and n is the order parameter which depends upon the mechanism of crystal growth.

In general the value of crystallization rate constant K increases exponentially with temperature. The temperature dependence behaviour of K indicates that the crystallization

of amorphous or amorphous glassy materials is a thermally activated process. Mathematically it can be expressed as

$$K = K_0 \exp (-E_c / RT) \quad (17)$$

Here E_c is the activation energy of crystallization, K_0 is the pre-exponential factor, R is the universal gas constant and T is the temperature. For isothermal condition parameters E_c and K_0 in Eq. (17) can be assumed practically independent of the temperature (at least in the temperature interval accessible in the calorimetric measurements).

In non-isothermal crystallization, it is assumed that the constant heating rate during the experiment. The relation between the sample temperature T and the heating rate β can be written as

$$T = T_i + \beta t \quad (18)$$

Here T_i is the initial temperature. The crystallization rate is obtained by taking the derivative of expression (1) with respect to time, keeping in mind that the reaction rate constant is a time function which represents Arrhenius temperature dependence.

$$(d\alpha/dt) = n (Kt)^{n-1} [K + (dK/dt) t] (1-\alpha) \quad (19)$$

The derivative of K with respect to time can be obtained from Eqs. (17) and (18), which follows as:

$$(dK/dt) = (dK/dT) (dT/dt) = (\beta E_c / RT^2) K \quad (20)$$

From Eq. (19) we obtained

$$(d\alpha/dt) = n K^{ntn-1} [1+at].(1-\alpha) \quad (21)$$

where $a = (\beta E_c / RT^2)$.

Using Eq. (21) Augis and Bennett (Augis & Bennett, 1978) have developed a crystallization kinetic method. They have taken proper account of the temperature dependence crystallization reaction rate. Their approximation results have also been verified the linear relation between $\ln (T_c - T_i)/\beta$ versus $1/T_c$ (here T_c is the onset crystallization or critical transition temperature). This can be deduced by substituting the u for Kt in Eq. (21), accordingly the rate of reaction can be expressed as

$$(d\alpha/dt) = n (du/dt) u^{(n-1)} (1-\alpha) \quad (22)$$

Where

$$(du/dt) = u [(1/t) + a] \quad (23)$$

Second derivatives of Eqs. (22) and (23) are given as:

$$(d^2\alpha/dt^2) = [(d^2u/dt^2) u - (du/dt)^2 \times (nu^2 - n + 1)] nu^{(n-2)} (1-\alpha) = 0 \quad (24)$$

$$(d^2u/dt^2) = (du/dt) [(1/t) + a] + u [(-1/t^2)] + (da/dt) \quad (25)$$

In Eq. (25) substituting for $(da/dt) = -(2\beta/T)a$, then it can be written as

$$(d^2u/dt^2) = u [a^2 + (2a T_i / tT)] \quad (26)$$

The last term in the above equation was omitted in the original derivation of Augis and Bennett [33] ($T_i \ll T$) and resulted in the simple form:

$$(d^2u/dt^2) = a^2 u \quad (27)$$

Substitution of (du/dt) and (d^2u/dt^2) in Eqs. (23), (27), and (24) gives the following expression:

$$(nu^{n-n+1}) = [at/(1+at)]^2. \quad (28)$$

For $E/RT \gg 1$, the right-hand bracket approaches its maximum limit and consequently u (at the peak) = 1, or

$$u = (Kt)_c = K_0 \exp (-E_c / RT_c) [(T_c - T_i) / \beta] \approx 1 \quad (29)$$

In logarithm form, for $T_i \ll T_c$

$$\ln (\beta/T_c) \approx (-E_c / RT_c) + \ln K_0 \quad (30)$$

Value of E_c and $K(T)$ can be obtained from the equation (30) by using the plots of $\ln \beta/T_c$ against $1/T_c$. Further, by using the Eq (17) Hu et.al. (Sbirrazzuoli, 1999) have introduced the crystallization rate constant stability criterion corresponding to T_c .

$$K (T_c) = K_0 \exp (- E_c / RT_c) \quad (31)$$

1.6 Differential Scanning Calorimetry (DSC) thermograms

Endothermic and exothermic peaks in amorphous glassy materials arise due to thermal relaxation from a state of higher enthalpy toward to metastable equilibrium states of lower enthalpy. The process of the thermal relaxation depends on temperature and may quite fast near the glass-transition temperature. The glass transition peak in DSC measurement represents the abrupt change in specific heat and decrease in viscosity (Matusita, 1984), while the crystallization peak demonstrate to the production of excess free-volume, and endothermic peak at T_m reflects the amount of energy which liberate owing to complete destroy the solid phase structure cause braking of all type existing bonds in solid alloy. Hence, the materials crystallizations temperatures as well as mode of crystallizations extensively depend on the compositions of alloys.

In general DSC thermograms of amorphous glassy (i.e. chalcogenide glasses) materials have exhibited a considerable shifts in endothermic glass-transition and exothermic crystallization temperatures with increasing heating rates. But in recent investigations (Singh & Singh, 2009) investigators have also been reported vary small or negligible endothermic glass transitions shifts in metal, semi-metal and non metal containing multicomponent chalcogenide glasses. In order to this, we have performed the DSC measurements on recent developed $\text{Se}_{93-x}\text{Zn}_2\text{Te}_5\text{In}_x$ ($0 \leq x \leq 10$) chalcogenide glasses.

These materials could be prepared by the well known most convenient melt quenched method. The high purity elements Selenium, Zinc, Tellurium and Indium were used. The suitable amounts of elements were weighed by electronic balance and put into clean quartz

ampoules (length of ampoules 8 cm and diameter 14 mm). All the ampoules were evacuated and sealed under at a vacuum of 10^{-5} Torr to avoid the reaction of glasses with oxygen at high temperature. A bunch of sealed ampoules was heated in electric furnace up to 1173K at a rate of 5-6 K/min and held at that temperature for 10-11 h. During the melting process ampoules were frequently rocked to ensure the homogeneity of molten materials. After achieving desired melting time, the ampoules with molten materials were frequently quenched into ice cooled water. Finally ingots of glassy materials were obtained by breaking the ampoules. The preparation and characterizations technique of the test materials also outlined in our past [Singh & Singh, 2010] research work.

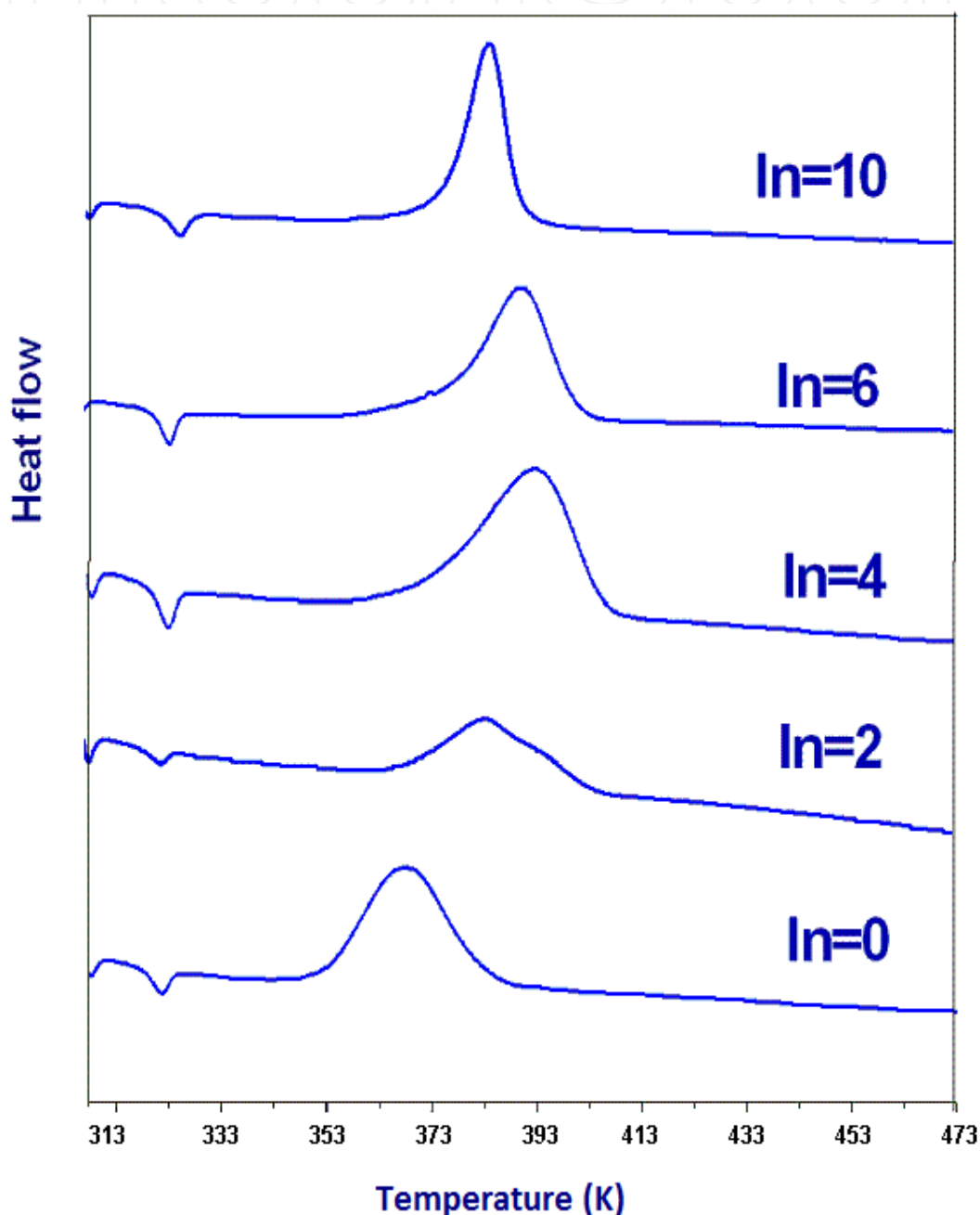


Fig. 1. DSC patterns of $\text{Se}_{93-x}\text{Zn}_2\text{Te}_5\text{In}_x$ ($0 \leq x \leq 10$) chalcogenide glasses at heating rate 5 K/min

DSC patterns of $\text{Se}_{93-x}\text{Zn}_2\text{Te}_5\text{In}_x$ ($0 \leq x \leq 10$) glasses at heating rate of 5 K (min)^{-1} is given in Figure.1. DSC traces clearly show the endothermic and exothermic phase reversal peaks at the glass transitions and crystallizations temperatures. Obtained values of the glass transitions temperatures (T_g), onset crystallizations temperatures (T_c), peak crystallizations temperatures (T_p) and melting temperatures (T_m) at heating rates of 5, 10, 15 and 20 K (min)^{-1} is listed in Table 1.

$\text{Se}_{93-x}\text{-Zn}_2\text{-Te}_5\text{-In}_x$ (X=0, 2, 4, 6 and 10)					
	Heating rate	T_g (K)	T_c (K)	T_p (K)	T_m (K)
$\text{Se}_{93}\text{-Zn}_2\text{-Te}_5$	5	318	354	368	501
	10	320	359	374	502
	15	322	363	378	503
	20	323	367	381	503
$\text{Se}_{91}\text{-Zn}_2\text{-Te}_5\text{-In}_2$	5	319	370	385	502
	10	322	376	392	503
	15	323	382	398	504
	20	324	385	402	504
$\text{Se}_{89}\text{-Zn}_2\text{-Te}_5\text{-In}_4$	5	319	372	393	503
	10	322	381	402	504
	15	324	385	407	504
	20	325	389	411	504
$\text{Se}_{87}\text{-Zn}_2\text{-Te}_5\text{-In}_6$	5	320	375	396	504
	10	323	383	405	504
	15	325	389	412	506
	20	327	392	415	506
$\text{Se}_{83}\text{-Zn}_2\text{-Te}_5\text{-In}_{10}$	5	319	370	386	504
	10	322	378	394	504
	15	323	383	400	504
	20	324	386	405	505

Table. 1 Obatined values of T_g , T_c , T_p and T_m at heating rates 5, 10, 15 and 20 K/min

Outcome demonstrates, a very small glass-transitions temperatures shifts and a considerable shifts in onset and peak crystallizations temperatures, the corresponding $T_c\text{-}T_g$ result is given in Figure.2 and their values listed in Table.2. This result revealed the values of T_c and T_p crystallizations temperatures increases upto 6 at. wt. % indium and beyond this decreased for 10 atomic percentage composition glass.

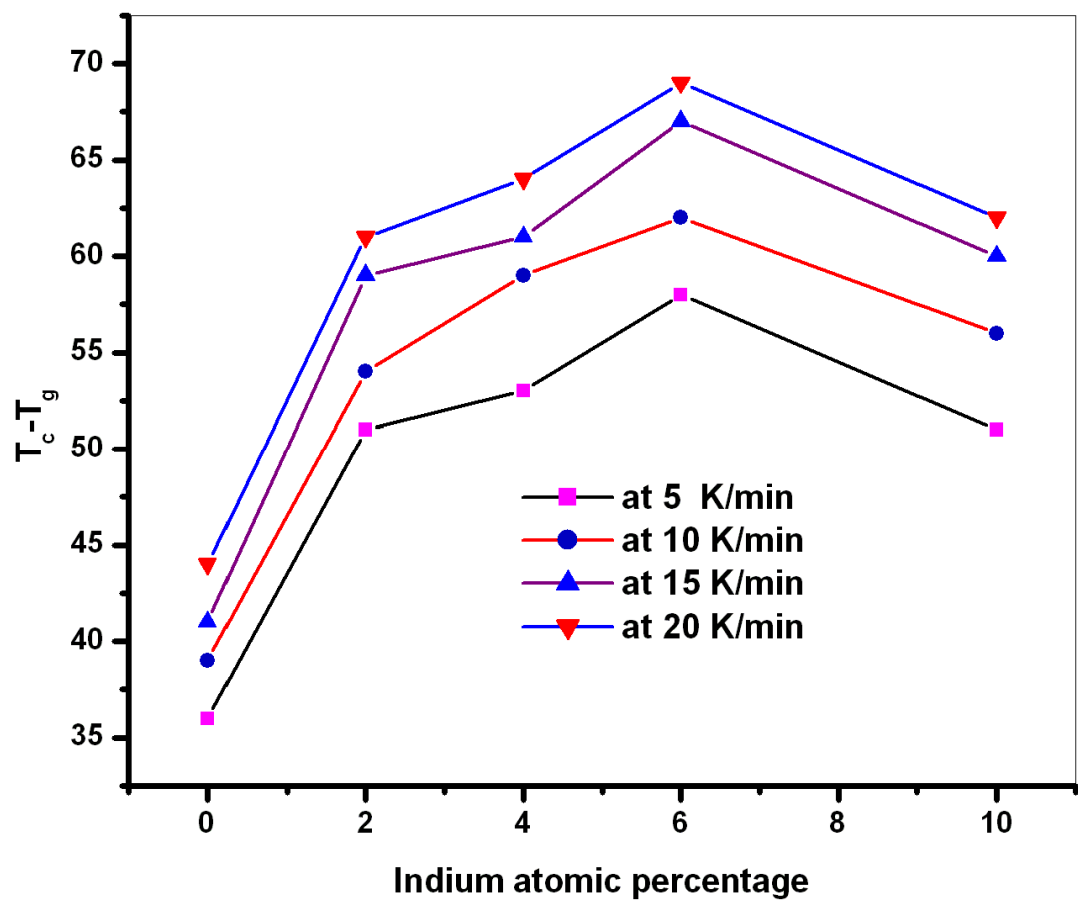


Fig. 2. Variations of $T_c - T_g$ with Indium atomic percentage at 5, 10, 15 and 20 K/min heating rates

	Heating rate	Se ₉₃ Zn ₂ Te ₅	Se ₉₁ Zn ₂ Te ₅ In ₂	Se ₈₉ Zn ₂ Te ₅ In ₄	Se ₈₇ Zn ₂ Te ₅ In ₆	Se ₈₃ Zn ₂ Te ₅ In ₁₀
$T_c - T_g$	5	36	51	53	55	51
	10	39	54	59	60	56
	15	41	59	61	64	60
	20	44	61	64	65	62
$T_p - T_c$	5	14	15	21	21	16
	10	15	16	21	22	16
	15	15	16	22	23	17
	20	14	17	22	23	19
$T_m - T_c$	5	147	132	131	126	134
	10	143	127	123	119	126
	15	140	122	119	114	121
	20	136	119	115	110	119

Table 2. Evaluated values of $T_c - T_g$, $T_p - T_c$ and $T_m - T_c$ at different heating rates

1.7 Glass forming ability (GFA)

GFA of material describes the relative ability to a set of compound adopt the amorphous structure (Mehta et al., 2006, Jain et al., 2009). In practice criteria to establish the GFA of vitreous materials are based on DSC measurements. Usually, unstable glass has show a crystallization peak near to the glass transition temperature while stable glass peak close to melting temperature. GFA can be evaluated by mean of the difference between the crystallization temperature (peak temperature T_p and/or onset temperature T_c) and the glass transition temperature (T_g). This difference varies with alloys concentrations and higher and lower for a certain composition. To evaluate the GFA of glassy alloys several quantitative methods have been introduced from the investigators. Most of the methods (Saad & Poulin, 1987, Dietzel, 1968) based on characteristics temperatures of glassy alloys. Dietzel (Dietzel, 1968) has introduced the first GFA criterion $D_T = T_c - T_g$. Further Hruby (Hruby, 1972) developed the H_R GFA criterion [$H_R = T_c - T_g / T_m - T_c$]. This method has additional advantage to describe the thermal stability of amorphous materials.

To applying the GFA criterion method, obtained critical characteristics temperatures difference $T_c - T_g$, $T_p - T_c$ and $T_m - T_c$ (Here T_g is glass transition temperature, T_p is peak crystallization temperature and T_m is the melting temperature) values of under examine materials is listed in Table 2. Using these values H_R parameter of GFA can be described as:

$$H_R = \left(\frac{T_c - T_g}{T_m - T_c} \right) \quad (32)$$

GFA variation with indium atomic weight percentage at heating rates 5, 10, 15 and 20 is given in Figure. 3 and their corresponding average values listed in Table 3. The higher GFA value is obtained for threshold indium concentration glass. High GFA value of threshold composition also reflects their high order thermal stability as compare to other glasses of this series.

1.8 Activation energy

Activation energy reflects the involvement of molecular motions and rearrangements of the atoms around the critical transitions temperatures (Suri et al., 2006). In DSC measurement atoms undergo infrequent transitions between the local (or metastable state) potential minima which separated from different energy barriers in the configuration space, where each local minima represent a different structure. The most stable configuration has local minima structure in glassy region. This literal meaning a glass atoms possessing minimum activation energy have a higher probability to jump in metastable state of lower internal energy configuration. This local minima configuration occurs at particular composition of alloy which refers as a most stable glass (Imran et al., 2001). The activations energies of chalcogenide glasses at the critical temperatures can be interpreted in these words: the glass transition activation energy (E_g), onset crystallization activation energy (E_c) and peak crystallization activation energy (E_p) are the amount of energies which absorbed by a group of atoms for a jump from one metastable state to another state (Imran et al., 2001, Agarwal et al., 1991).

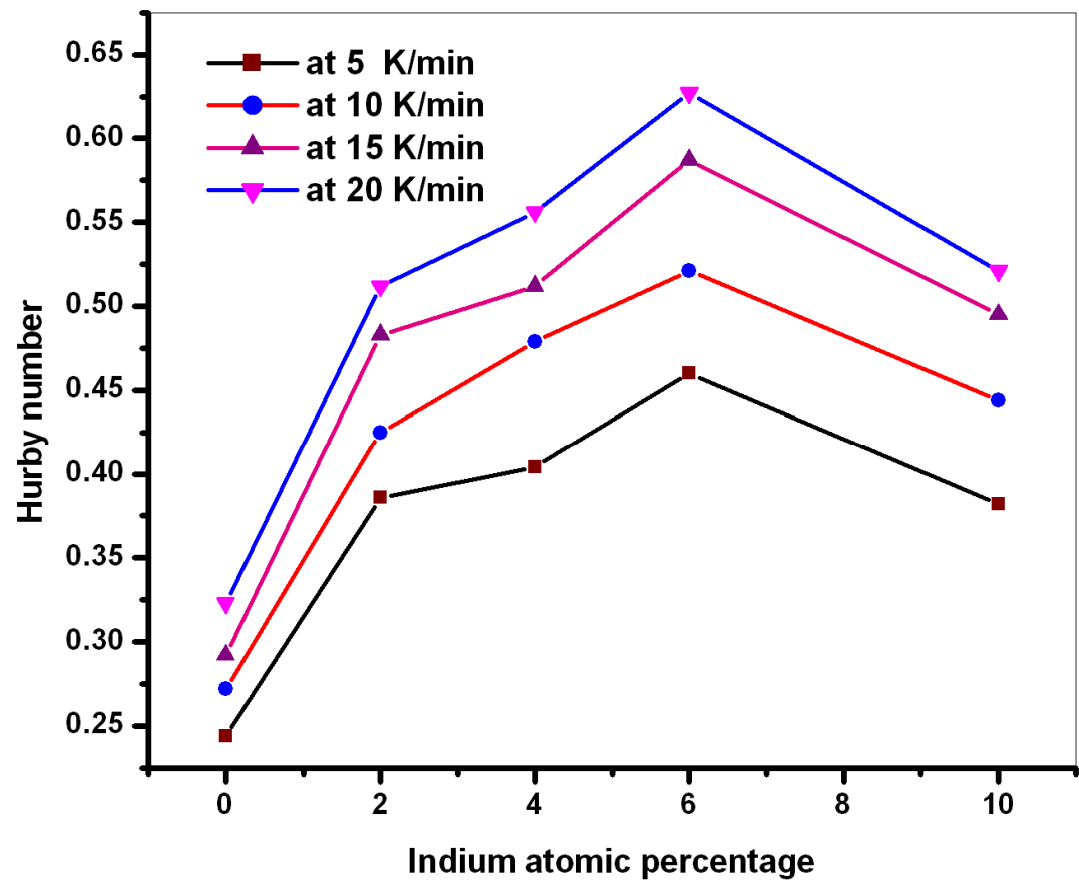


Fig. 3. Plots of GFA parameter with indium atomic percentage at 5, 10, 15 and 20 K/min heating rates

1.8.1 Glass transition activation energy

The glass transition activation reflects the endothermic energy of the material which produced due to unsaturated or hydrogen like bond braking at the pre-crystallization critical temperature. Glass transitions activations energies of the under test glasses can be defined by using Ozawa method (Ozawa, 1970).

$$\ln \beta = - \left(\frac{E_g}{RT_g} \right) + C \tag{33}$$

where β is the heating rate, E_g is the glass transition activation energy, C is the constant in usual meaning. Obtained Ozawa plots, $\ln \beta$ vs $1000/T_g$, for these materials is given in Figure.4 and their corresponding E_g values is listed in Table 3.

Outcomes revel the E_g values have a maxima and a minima for 0 and 6 percentage indium compositions glasses. Thus the E_g values have very small increasing and decreasing trend in T_g values (see Table 3&Table 1) with increasing DSC heating rates in these metal, semi-metal and non-metal containing multicomponent chalcogenide glasses. The high activations energies at pre-crystallizations reflect the materials rigidity. While, normally reported T_g values for non-metallic chalcogenides compositions has show a considerable shifts with

DSC heating rates. Hence the obtained T_g values results in increasing DSC heating rates for metal, semi-metal and non-metal containing multicomponent chalcogenide glasses are not in good agreement with previous reported non metallic compositions. Deviations in the results arise due to existence relatively hard metallic, semi-metallic characters unsaturated bonds with hydrogen like week bonds in the alloys stoichiometrics. Further, it is quite possible to large amount of metallic, semi-metallic characters unsaturated bonds sustain over to T_g critical transition temperature of the materials owing to requirement greater amount of energy to bark the heteropolar unsaturated bonds. As consequence the metal,

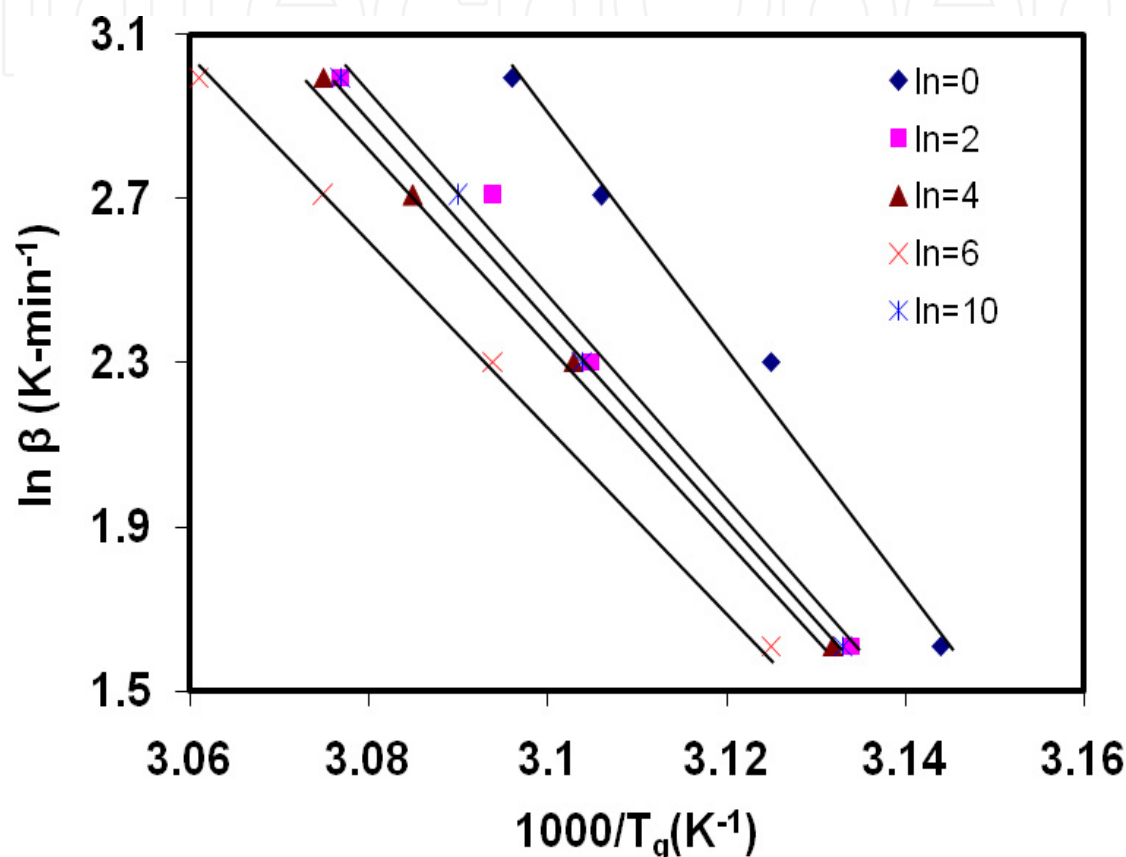


Fig. 4. Ozwa polts of $Se_{93-x}Zn_2Te_5In_x$ ($0 \leq X \leq 10$) glasses to obtain E_g

$Se_{93-x}Zn_2Te_5In_x$ ($X=0, 2, 4, 6$ and 10)				
Alloy compositions	Glass transition activation energy E_g (KJ/mol)	Onset crystallization activation energy E_c (KJ/mol)	Peak crystallization activation energy E_p (KJ/mol)	Average (GFA)
$Se_{93}Zn_2Te_5$	229.94	115.64	118.23	0.282
$Se_{91}Zn_2Te_5In_2$	205.02	106.11	96.40	0.451
$Se_{89}Zn_2Te_5In_4$	195.47	99.02	91.09	0.487
$Se_{87}Zn_2Te_5In_6$	174.23	93.66	82.77	0.548
$Se_{83}Zn_2Te_5In_{10}$	199.88	101.84	92.70	0.460

Table 3. E_g , E_c , E_p and GFA values of $Se_{93-x}Zn_2Te_5In_x$ ($0 \leq x \leq 10$) chalcogenide glasses

semi-metal and non-metal containing multicomponent chalcogenide glasses have exhibited either very small or negligible glass transitions temperatures shifts with increasing DSC heating rates.

1.8.2 Onset crystallization activation energy

Onset crystallization activation energy (E_c) is the amount of thermal energy which requires to begin the phase transformation from glassy to crystallization state. Quantitative knowledge of onset crystallization activation energy at T_c defines the heat/energy storage capability of the material which useful for different physical applications. The exothermic onset crystallization activation energy at T_c arises due to barking of existing covalent bonds in glassy configuration. In case of complex metallic multicomponent chalcogenide glasses high energy homopolar and heteropolar covalent bonds formed as compare to metallic binary and ternary compositions. Due to this the critical onset crystallization temperatures of the complex metallic glasses (see Table 1&Table 3) increases and their corresponding activation energies tend to be decrease upto threshold composition then visa-verse direction. While in case of non-metallic binary, ternary and multicomponet chalcogenide alloys reports demonstrated they have lower values of onset crystallizations temperatures owing to existence of week homopolar and heteropolar bonds in glassy configuration.

Onset crystallizations activations energies of under examine complex metallic multicomponent chalcogenide glasses described by employing the Ozawa method (Ozawa, 1970).

$$\ln \beta = -\left(\frac{E_c}{RT_c}\right) + C \quad (34)$$

Here symbols (β is heating rate, E_c is the onset crystallization activation energy, T_c is the onset crystallization temperature and R & C are the constant) are in usual meaning. Obtained Ozawa plots $\ln \beta$ vs $1000/T_c$ is given in Figure. 5 and their corresponding E_c values is listed in Table 3. Outcomes show a phase reversal in E_c values which have a maxima and minima corresponding to 0 and 6 atomic weight percentage of indium glasses.

1.8.3 Peak crystallization activation energy

Peak crystallization activation energy (E_p) of a glass expresses the amount of heat energy which requires for utmost crystallization. By mean at peak crystallization point almost all the existing heteropolar covalent bonds have to be broken and material achieve to maximum crystallization i.e. a glassy phase material completely transform to crystalline phase and relax toward to original state. The E_p values of examined materials can be described by using the Kissinger method (Kissinger,1957).

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_p}{RT_p} + C \quad (35)$$

Here symbols (β is heating rate, E_p is the peak crystallization activation energy, T_p is the paek crystallization temperature and R & C are the constant) are in usual meaning. Obtained E_p values from Kissinger plots (see Figure. 6) are listed in Table.3.

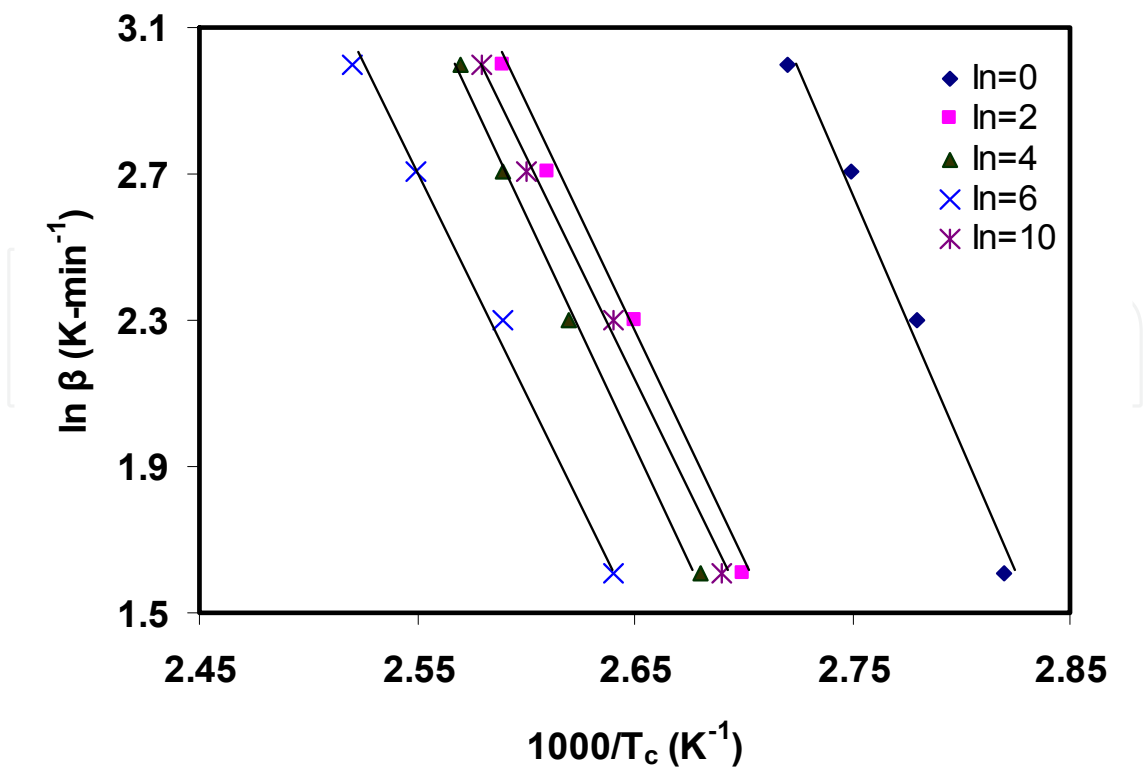


Fig. 5. Ozwa polts of $\text{Se}_{93-x}\text{-Zn}_2\text{-Te}_5\text{-In}_x$ ($0 \leq X \leq 10$) glasses to obtain E_c

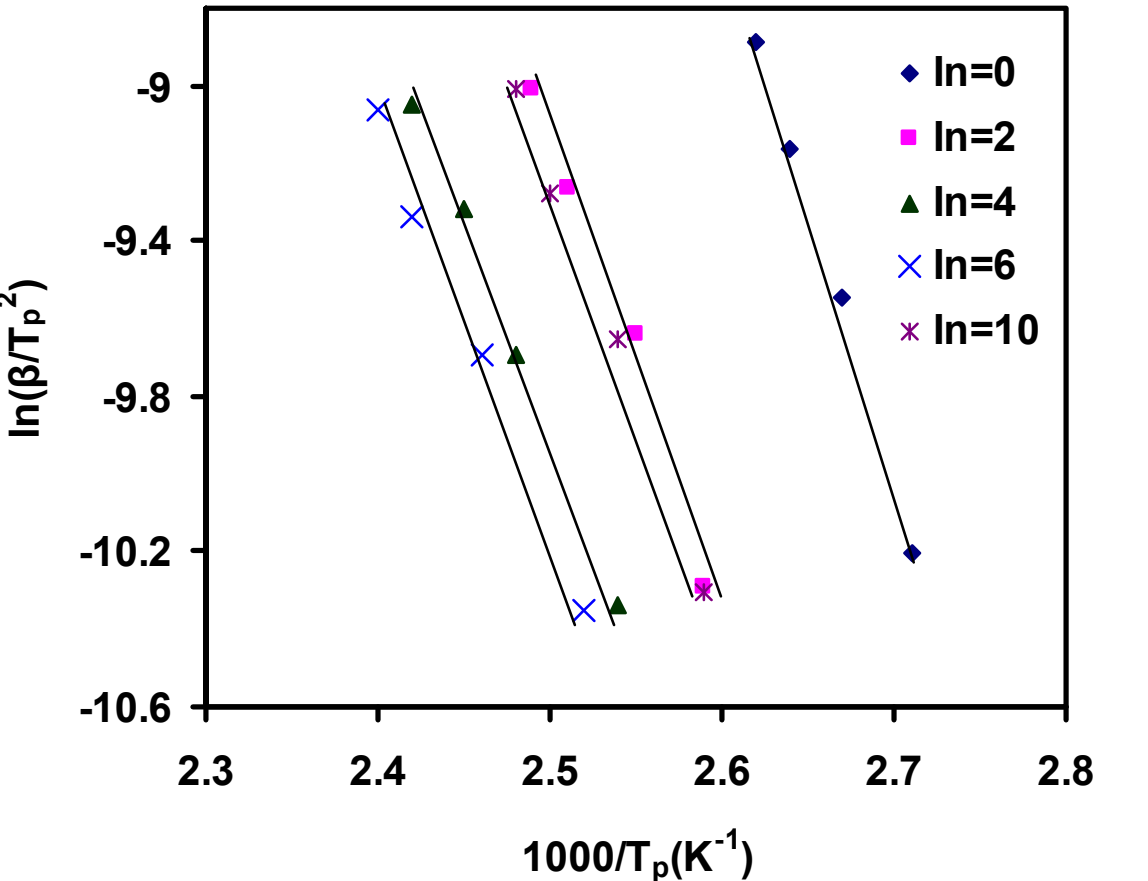


Fig. 6. Kissinger polts of $\text{Se}_{93-x}\text{-Zn}_2\text{-Te}_5\text{-In}_x$ ($0 \leq X \leq 10$) glasses to obtain E_p

Values of E_p also show a phase reversal with alloying compositions and have a maxima and minima respectively for 0 and 6 atomic weight of indium. Commonly, in metal, semimetal and non-metallic elements containing multicomponent chalcogenides show a sharp and continuous crystallization process (exception is also reported in few composition of chalcogenide glasses) with lower E_p values. The sharp crystallization prevail between T_c (where crystallization began) and T_p (where crystallization completed) owing to continuous breaking of rigid heteropolar bonds cause generation of greater amount of heat energy in the specimen.

1.9 Melting temperature (T_m)

Melting temperature of amorphous glassy materials defines as; temperature at which solid state materials destroy all the existing homopolar and heteropolar bonds and alloying elements separated. Melting temperatures of amorphous glassy materials extensively depend on the constituent of the alloys. Technologically kinetics at T_m have less importance, therefore investigators interest to provide only introductory information regarding to phase transformation at T_m in amorphous glassy materials.

2. Discussions

Crystallizations kinetics variations in under test metal, semi-metal and non-metal containing multicomponent chalcogenide glasses can be interpreted in term of bond formation in solids. It is expected to Zn and Te dissolved in Se chains and makes Zn-Zn, Te-Te, Se-Se, Se-Zn, Se-Te, Se-Zn-Te homopolar and heteropolar bonds. Essentially ternary Se-Zn-Te glass can forms cross-link heteropolar metastable state structure. The heteropolar bonds will be produced the defects in density of localized state owing to existence of dangling bonds in alloy configuration (Maharjan et al., 2000, Saffarini, 2002, Abdel Latif, 1998). Further incorporation of foreign element Te concentration in ternary configuration transforms the whole stoichiometry into quaternary or multicomponent system. The metal, semi-metal and non-metal multicomponent glassy configuration possibly makes them dominating Se-In heteropolar bonds with other metallic character bonds Zn-In, Te-In. The Se-In heteropolar bonds play an important role in crystallization kinetics variations due to fixed amounts of Zn and Te. Addition of additional indium concentration has produced the heavily cross-linked structure in which steric hindrance increases. Therefore the expanse of Se chains and replacement of weak Se-Se bonds by Se-In bonds results the increase and decrease in associative activations energies. A chemical threshold has established at critical composition (6 at wt % of In). At this concentration glassy structure become more chemically ordered and contains large number of Se-In bonds (Singh, 2011). As consequence a significant change is appeared in crystallization parameters of threshold composition alloy.

Furthermore, incorporation of indium concentration beyond the threshold composition reduced the Se-In bonds and increases the In-In bond strength in glassy configuration. The increase and decrease bonds strengths of Se-In and In-In influenced the defects / dangling bonds concentrations in the glassy stoichiometry. Owing to alternation in dangling bonds densities the GFA, activations energies E_g , E_c and E_p of the corresponding glass show a significant change in kinetic parameters.

3. Summary

In summary, in this work an effort is made to present the fundamentals (in short form) of nucleation and growth processes and crystallization in amorphous glassy (chalcogenide glasses) materials. Further, project a clear view on natural crystallization and process of non-isothermal crystallization kinetics of chalcogenide glasses. Subsequently a concrete explanation on origin of endothermic and exothermic peaks in DSC measurements is also discussed. Glass forming ability and crystallizations kinetics of recent developed $\text{Se}_{93-x}\text{Zn}_2\text{Te}_5\text{In}_x$ ($0 \leq x \leq 10$) metal, semi-metal and non-metal containing multicomponent chalcogenide glasses have also been taken under discussion. Outcomes revealed such combinations glasses have high order GFA and thermal stability and low E_c , E_p activations energies as compare to previous reported non-metallic compositions. In subsequent it has found these materials critical kinetic parameters extensively depend on their alloys constituents and have a maxima and a minima in respective manor for threshold composition glass. It is also concluded that the crystallizations kinetics variations in these glasses can be occur owing to fluctuations in solid state bonds densities in localized states. In case of metallic multicomponent chalcogenide glasses heteropolar unsaturated and covalent bonds may play an important role in crystallization kinetics variations.

Indeed, chalcogenide glasses are the potential materials which used in various optoelectronics applications, but still have plenty of room for their applications in different areas which have either less studied or undiscovered. A few thrust areas of these materials are outlined here in which they have (or may have) potential applications. Surface plasmon resonance (SPR) is a very versatile and accurate technique to determining small changes in optoelectronics parameters like, refractive index at the interface of a metal layer and the adjacent dielectric medium. The SPR detection mechanism has secured a very important place among several sensing techniques due to its better performance and reliable procedure. Chalcogenide materials can also perform as infrared sensing for an efficient, non-destructive and highly selective technique in detection of organic and biological species. This technique has combined benefits of ATR spectroscopy with the flexibility of using a fiber as the transmission line of the optical signal, which allows for remote analysis during field measurements or in clinical environments. Sensing mechanism based on absorption of the evanescent electric field, which propagates outside the surface of the fiber and interacts with any absorbing species at the fiber interface. However, their efficiency controlled multilayer optical filters by periodically switching and evaporation angle, leading to periodic dielectric structure makes them a potential candidate for chemical sensing application. Further, their larger refractive index amongst the glasses makes them to made chalcogenide based ultra-low loss waveguides devices. Chalcogenide materials have most promising applications in area of phase change memory (PCM) and in photonics. Their unique physical characteristic the reversible amorphous to crystalline phase change which can be induced by controlled thermal cycling (through laser absorption or current flow) in certain chalcogenide alloys. Phase-change materials have always technological importance to make read-write storage device (commercially rewritable CD/DVD), because they can be switched (in nanoseconds) rapidly back and forth between amorphous and crystalline phases by applying appropriate laser heat pulses. Although optical phase-change storage is a widespread and successful technology, further advances in areal densities will be very challenging. Moreover, chalcogenide (in glassy or nano embedded) based photovoltaic cells

applications are also identified as a prominent alternative of conventional energy which can provides terawatts capacity at cheaper cost. But improvement in low efficiency chalcogenide based photovoltaics is challenging in future. Thus, in view of author glassy and nano embedded (glassy) chalcogenides would be matter of future research to undersatnd the molecular /- or nano-phase photonics of the materials, particularly for thrust areas in PCM memory and photovoltaics applications. In author opinion chalcogenide glasses (bulk or nano phase) has a bright future and it is still open for further inventions.

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