CHAPTER 7

CRYSTALLISATION OF ARSENIC SELENO IODIDE GLASS
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7.1 Introduction

In the recent years, amorphous to crystalline transformations and the associated changes in electrical properties have received intensive attentions as they are believed to be directly related to the memory switching phenomena observed in amorphous semiconductors. With the emerging potential of this type of phenomena, the basic aspects of the vitreous state and their relationship to the crystalline state are now the subject of world wide fundamental studies. An intensive research in arsenic chalcogenide glasses is due to both the structural features and the relatively small values of the melting points which permit supercooling of the corresponding melts easily and also obtaining glasses of complex composition.

Chalcogenide glasses are of considerable interest owing to their practical use for recording optical information in the visible and near IR region of the spectrum, computer memories and for modulating laser emission etc., [1-4].

7.2 Chalcogenide glasses

In contrast to crystalline solids and to liquids (even if undercooled) glass is in a nonequilibrium state. Transition from the liquid to the glassy state and back are not thermodynamic in character. They are relaxation process [5-6]. The structure of glass, roughly speaking corresponds to equilibrium at a temperature above the experimental temperature (higher than Tg). In other words, the structure of glass is a frozen liquid structure. This is true for glasses of any
composition, inorganic glasses, polymers and vitrified liquids of low molecular weight. The quasicrystalline nature of liquids and the existence of short-range order with simultaneous absence of long-range order in them. The secondary difference between the structure of glasses and melts is that in a liquid the structure is continuously reformed as the temperature changes and the short-range characteristic acter with temperature [7]. The kinetic properties of a liquid cannot be characterised by a single relaxation time but there is a range of relaxation times corresponding to different degrees of freedom of kinetic units and their combinations. Moreover, the concept of degree of freedom of a kinetic unit itself loses any direct meaning for a liquid as any movements in it are cooperative processes. It is evident that different configurational variations must take place at different Tg; therefore these is a vitrification range rather than a point. The process which determine the macrostate of the system are frozen in a glass. At the same time a glass retains the ability to undergo definite microarrangements. The structure of glass must be very close to the structure of most, but not identical with it. Vitrification is due to intermolecular and interatomic forces which differ in different substances, for eg. hydrogen bonds in alcohols, peculiar chemical bonds in inorganic glassy materials, Van der Walls forces in polymeric hydrocarbons, etc. vitrification consists of freezing of the equilibrium between forming and dissociating bonds.

7.2.1 Binary Chalcogenides

Sulphur, selenium phospho-nitrochloride and phosphonitro fluoride [6] form glasses and these glasses are called chalcogenide glasses [7], distinguished from the oxide
type of glasses by their high electronic conductivity and absence of ionic conductivity. They constitute an extensive group of materials whose, optical, electrical and other properties vary with composition within a fairly wide range. They are all semiconductors whose distinctive features are the absence of long-range order, their homogeneity, the independence of their properties on small amounts of impurities and small mobility of charge carriers. Tellurium glass can be obtained only by condensation of vapour [5]. The presence of elements like As, Sb, Si and Ge with chalcogens aids glass formation [5]. The extreme cross-linking of these elements in the glass crystalline states makes mobility of the atoms impossible so that melting can occur only with a structure transformation. The glass formation is a more difficult as the atoms become heavier because the bonds which involve in heavier atoms are generally weaker so that easy dissociation and rearrangement of the atoms into a crystal lattice can occur. The heavy atoms can loosely bound atoms in addition to those atoms corresponding to the valence which are tightly bound. At higher temperature and especially in the melt: tightly and loosely bound atoms can easily be interchanged so that the reference atom may move away from a near neighbour and another one comes closer. This is approximately equivalent to the breaking of a strong bond and the formation of a new one. In this way the rearrangement of atoms and hence the crystallization is possible. The composition of chalcogenide glasses can be varied within wide limits. However, in the systems As-Se and As-S. As content cannot go over 60 atomic percent, while glassy region on the chalcogenide side, goes upto 100 atomic percent of Se and about 90 atomic percent of S [8,9].
7.2.2 Ternary Chalcogenides

Ternary chalcogenide glasses are generally obtained by simply melting the components and cooling [10]. Flashen et al [11] have reported the new family of glasses in ternary system of arsenic, sulphur and iodine. These glasses have low melting points and exhibit good chemical durability. They are insoluble in water, acids including HF and weak bases. They decompose in strong alkali and among oxidizing agents. Glasses of high sulphur content show surface hydrolysis in boiling water. The structure of these glasses is based upon extended chains involving polymeric \((-S-S)_n\) bonding, the role of iodine species being one of a chain terminator. The other systems of As-S-x(x=Cl,Br) also have wide glass formation regions [12]. The glass formation region of SbSI [13] and SbSBr [14] has also been investigated. Chalcogendie semiconducting glasses of the system As-Te-I have also been reported [15].

In the previous Chapters (Chap. 2-6) the authors has dealt extensively with the growth of single crystals from vapour. Except antimony and bismuth chalcohalides in the V-VI-VII group, arsenic chalcohalides and chalcogenides have greater tendency to form glasses. Because of their glass forming tendency, the ternary chalcohalides of arsenic have been less studied in the crystalline state. There are reports in literature on ternary systems of As-X-Y (X = S, Se, Te and Y = Cl, Br, I) giving glass forming regions [11, 12]. But the crystallization behaviour of arsenic chalcohalides like AsSI, AsSeI, AsTeI has not been studied in detail. So in the present chapter, the author deals with the crystallization behaviour of AsSeI glass by isothermal annealing [16].

7.3 Arsenic Seleno iodide

Arsenic seleno iodide is a semiconductor with energy gap of 1.87 eV[17]. The analyses of the quasi-binary systems
of $\text{As}_2\text{Te}_3$ - $\text{AsI}_3$ [18] and $\text{As}_2\text{Se}_3$ - $\text{AsI}_3$ revealed thermodynamically stable phases like $\text{As}_4\text{Te}_5\text{I}_2$, $-\text{AsTeI}$ and $-\text{AsSeI}$. In addition to that, metastable phases like $-\text{AsTeI}$ and $-\text{AsSeI}$ have also been observed [19]. Monoclinic $\text{As}_5\text{Te}_4\text{I}$ crystals grown hydrothermally have also been reported [20]. The growth of single crystals of these compounds is difficult due to the tendency of easy glass formation. The $-\text{AsSeI}$ crystals are dark red in transmitted light and metallic in character in reflected light. $-\text{AsSeI}$ belongs to monoclinic system with $a = 0.8855(20)$ nm, $b = 0.4194(1)$ nm, $c = 0.9792(1)$ nm and $\beta = 93.74(1)^\circ$ and has four molecules per unit cell with the space group $P2_1$. $-\text{AsSeI}$ is cubic with $a = 1.105$ nm and has 16 molecules per unit cell belonging to the space group $F4_132$ [19].

The structure of $\text{AsSeI}$ consists of chains of $\text{AsSe}_2\text{I}_2$ trigonal pyramids. The pyramid is the structural cause of the chain, and arsenic atom is located at the apex of the triangle at the base of the pyramid. The pyramids are joined by a selenium atom (figure 7.1). But the structure of $\text{SbSI}$ consists of chains of composition ($\text{Sb}_2\text{S}_2\text{I}_2)_n$ running parallel to the c-axis (chapter 4). So in general, structure of $\text{AsSeI}$ can be regarded as entirely different from antimony sulfide iodide structure. The phase diagram of the system of $\text{AsSe-I}$ [21] is shown in figure 7.2. The melting point of $\text{AsSeI}$ is 221°C. The phase diagram of the partial system of $\text{AsSe-I}$ in the glassy region (approx. 45 atomic % of iodine) is eutectic type. $\text{AsSe}$ crystallizes first in the hypoecutetic region owing to predominance of $\text{As}_2\text{Se}_4$ structural units in these glasses. The primary phase crystallizing in the hypoeutectic alloys in $\text{AsSeI}$ and these glasses consist mainly of three component structural units.
Fig. 7.1

Chains of As-Se-I pyramids in the As-Se-I structure.
7.4 Experimental

The initial compound was prepared from elements of arsenic (99.999%), selenium (99.99%) and analar grade (99.9%) resublimed iodine. They were mixed in the stoichiometric ratio, in a glass ampoule and sealed at a pressure of $10^{-4}$ Torr. The ampoule was kept in a furnace initially at 200°C for two weeks and then raised slowly at the rate of 2-5°C per hour to 450°C and kept at 140°C - 170°C (which is the softening temperature for vitreous AsSeI [21]), for several months.

7.5 Results and discussion

Crystallization behaviour was investigated by taking X-ray powder diffractogram using CuK radiation for different periods of isothermal annealing. Figure 7.2 shows the X-ray analysis of glassy AsSeI after 5 months of annealing. According to Mikhailov et al [21], the crystallization tendency of AsSeI$_{XY}$ glasses is low and the crystallization tendency depends to a considerable extent on the arsenic-selenium ratio. Glasses having relatively high iodine contents crystallize with comparative ease. The glass forming tendency increase in the As-Se-I system, at high selenium contents (Se : As $\geq$ 9) and indicates the predominant interaction of iodine with arsenic when iodine is introduced into arsenic selenide glasses. When iodine is introduced into glassy alloys (Se:As = 0.8-1.05) the three dimensional As$_4$S$_4$ tetrahedra and trigonal AsSe$_3$ structural units constituting arsenic selenide glasses are partially transformed into three component structural units, without change in the continuity of the structure [21]. Figure 7.4 is the X-ray powder pattern after 7 months of annealing. From the powder diagram we can see that -AsSeI is the major constituent and in addition to that we have metastable phases -AsSeI and
Fig. 7.3
Fig. 7.4
As$_2$Se$_3$. Figure 1 (7.1) shows the scanning electron micrograph of the surface of the crystallized AsSeI after 7 months of annealing. It shows crystallites of varying grain sizes. Since crystallization of glassy melt is a time consuming process due to the low mobility of the atoms in such a highly viscous melts; the growth rates are extremely small resulting in longer growth periods. So it is possible to produce micro-crystalline particles by heating the glassy material for a longer period of time at an optimum temperature or softening temperature so that glass can be devitrified. Glass ceramics [22,23] are also prepared in this way by a suitable heat treatment controlling nucleation and thereby crystal growth. This micro-crystalline material with more or less coarse grains can be obtained by starting this schedule at the equilibrium temperature which is more convenient to proceed. The grains as shown in figure 1 (plate 7.1) are densely packed and the average grain size is approximately two to four microns. The crystallization normally occurs from the surface of the glass, i.e. nucleation is achieved at the surface where there is sufficient energy to overcome the barrier to nucleation. When a glass devitrifies by surface crystallization [23] there is a strong orientation effect and the crystals formed at the surface tend to show a coarse grained structure. It is evident from the X-ray powder analysis (figure 4) that both As$_2$Se$_3$ and AsSeI crystallize out along with the major constituent AsSeI. So with the initially formed nuclei, more nucleations occur which act as autocatalyst. During isothermal annealing the cubic AsSeI (metastable) transforms into AsSeI due to ordering [19]. Figure 2 (plate 7.2) shows the surface of the crystallized AsSeI after 8 months of annealing. It depicts the grains with an approximate size of 20 to 30 microns. The grains are irregular in shape, because prolonged heating exhibits grain growth whose rate is a function of time and temperature. The grain size will increase with increase of
of time due to the coalescence of grains [24]. Figure 3 (plate 7.1) shows the surface after 9 months of annealing where the size of the grain is large due to the aforesaid reasons. But further annealing (7-10 months) yielded an entirely different surface morphology, containing pits. The pits are of varying depths (figure 4, plate 7.1) on an average, approximately 100 microns. Because of the surface crystallization as already mentioned, surface orientation tend to produce weak spots on the surface due to the severe distortions from the viscosity of the interior glass and so pits or fractures perpendicular to the surface occur. The grain morphology within the pits (figure 1 plate 7.2) and outside the pits (figure 2, plate 7.2) is somewhat different. Figure 7.5 shows the X-ray powder pattern after ten months of annealing. The -AsSeI phases and \( \text{As}_2\text{Se}_3 \) phases disappear after prolonged isothermal annealing [4, 19].

The crystallized polycrystal was reddish black in colour (Fig. 3, plate 7.2). The presence of arsenic, selenium and iodine was confirmed by the homogeneous distribution the emission spots and the arsenic X-ray emission map is as shown in figure 4 (plate 7.2). Chemical analysis by photometric method [25] revealed stoichiometric composition with an accuracy of 4.1.

7.6 Conclusion

In the case of non-stoichiometric AsSeI glasses, crystallization occurs after prolonged annealing. For AsSeI\(_x\)I\(_y\) glasses, crystallization occurred only after a long duration of annealing, the annealing time for these glasses ranged from one month to ten months [21]. Glasses with approximately equal constants of arsenic and selenium are resistant to crystallization.
and in system, As-Se-I, the influence of iodine on crystallization depends on arsenic-selenium ratio. So during isothermal annealing of stoichiometric AsSeI glass, crystallization starts occurring only after five months and $-\text{AsSeI}$ and $\text{As}_2\text{Se}_3$ phases crystallize out along with the major constituent $-\text{AsSeI}$. But, after prolonged isothermal annealing the metastable phase $-\text{AsSeI}$ transforms to $-\text{AsSeI}$ which is stable.
LIST OF REFERENCES


