5.1 Introduction

The halide and chalcogenide glasses have received a great deal of interest as potential candidates for materials transmitting in the mid-infrared region (Baldwin et al., 1981; Poulain, 1983). However, they have relatively high refractive indices (Kothiyal et al., 2007) and give rise to large intrinsic losses in mid-infrared. There is a third family of infrared transmitting glasses prepared with mixtures of chalcogenides and halides known as chalcohalides. The halide glasses have received much attention because of their excellent property of mid and far infrared (IR) transmission (Drexhage, 1985; Lucas, 1986; Ding et al., 1986). These glasses are good candidates for application in CO₂ laser fibers and infrared windows, especially in medical applications (Nishii et al., 1989). In this chapter we discuss the preparation of chalcohalide \( \{x\text{Sb}_2\text{Se}_3(1-x)\text{CuI}\} \) glass by melt quench technique and report measurement of thermo-physical and optical properties as well as sub-micro structural features of these glasses. We also discuss the structural/structural units of these glasses by X-Ray Diffraction (XRD) and Neutron Diffraction (ND).

5.2 Experimental Investigations

The chalcohalide glass preparation by using rocking furnace and to know the nature of samples the characterization were done by using different tools such as XRD, ND, FTIR, UV-Vis, DTA, microhardness, I-V Characteristics (switching memory) and density etc.

5.2.1 Glass Preparation

Samples of the \( \text{Sb}_2\text{Se}_3(\text{CuI}) \) pseudo-ternary glass were prepared by well-established melt-quenching technique. The preparation was carried out in a specially
designed quartz ampoule by taking predetermined quantities of high purity raw materials of Antimony (Sb), Selenium (Se) and copper iodide (CuI). The initial charge is then sealed in quartz ampoules under vacuum of $10^5$ torr. The ampoule along with charge is placed in the quartz tube in a rocking furnace and heated in a programmed manner to a temperature of $850^\circ$C-$900^\circ$C for a period of 16-20hrs. The furnace is then held in vertical position without rocking and maintained at this temperature for about 6-8hrs. Then the quartz ampoule along with the melt is taken out of the furnace and quenched in air; the quenching conditions were optimized to obtain the crack free glass discs. The ampoule is then broken open to remove the glass samples.

Table 5.1: Batch compositions and appearance of melted samples

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Name of Samples</th>
<th>Chemical Composition Mol%</th>
<th>Melt Temperature ($^\circ$C)</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SSCI-1</td>
<td>50%Sb$_2$Se$_3$-50%CuI</td>
<td>850</td>
<td>Partial</td>
</tr>
<tr>
<td>2</td>
<td>SSCI-2</td>
<td>60%Sb$_2$Se$_3$-40%CuI</td>
<td>850</td>
<td>Glass</td>
</tr>
<tr>
<td>3</td>
<td>SSCI-3</td>
<td>30%Sb$_2$Se$_3$-70%CuI</td>
<td>850</td>
<td>Partial</td>
</tr>
<tr>
<td>4</td>
<td>SSCI-4</td>
<td>40%Sb$_2$Se$_3$-60%CuI</td>
<td>850</td>
<td>Glass</td>
</tr>
</tbody>
</table>

5.2.2 Characterization of the Samples

We used XRD and Neutron Diffraction for characterization of the glass samples as discussed in the earlier Chapter.

5.2.2.1 XRD Analysis:

We made structural analysis of the glass samples employing XRD and ND. The XRD plots for the various samples are shown in Fig. 5.1 and Fig. 5.2. The amorphous i.e., glassy nature of the samples is confirmed by the presence of broad peaks in X-ray diffraction patterns. The SSCI-2 and SSCI-4 show the glassy nature and other two samples namely SSCI-1 and SSCI-3 show partial crystallization.
Similarly broad peak in XRD pattern of sample SSCI4 confirms the glassy nature of the prepared samples. As sample SSCI-4 has shown glassy nature. We further carried out ND analysis for this sample.
5.2.2.2 Neutron Diffraction Analysis

We have done neutron diffraction (ND) studies on the sample $0.4\text{Sb}_2\text{Se}_3-0.6\text{CuI}$ on the High-Q diffractometer at the Dhruva reactor, BARC, Mumbai India, to understand the short range order and network connectivity. The measured scattering intensities were divided by monitor spectra, normalized on the scattering from standard vanadium bar and corrected for absorption, multiple scattering, self-shielding, and scattering from the container (Egelstaff, 1987). The data was transformed into real space to obtain the total correlation function, $T(r)$ of this sample using Monte Carlo $G(r)$ method as the S(Q) data is finite in Q (Ramesh et al., 1998). The structure factor S(Q) vs. scattering wave vector Q is as shown in Fig. 5.3 and total pair correlation function $T(r)=4\pi\rho g(r)$ vs. $r$ in Fig. 5.4.

![Fig. 5.3: Total structure factor S(Q) v/s Scattering wave vector Q](image)

![Fig. 5.4: Total correlation function T(r) v/s. r](image)
We have further measured density and microhardness.

5.2.3 Density Measurements

The density of the glass sample is determined by the Archimede’s method as mentioned earlier using xylene/water as an immersion liquid. The values are given in Table 5.2. The density measured at 20°C by Archimedes method was found to be 5.59 gm/cc with an accuracy of +/-0.5%. The densities of chalcogenide and chalcohalide are higher than that of the oxide glasses.

5.2.4 Microhardness Measurements

The Microhardness was determined by indentation technique using Vickers indenter on a Microhardness tester as mentioned. Indentation loads between 10g and 50g were used with the dwell of 5 s. A typical indentation on the SSCI-4 sample is shown in Fig. 5.6. The microhardness values are given in Table 5.2. The microhardness of glass is found to be 108.8 kg/mm² with standard deviation of 4.8kg/mm².

Fig. 5.6: A typical indentation on the SSCI-4 glass
5.2.5 Thermo-Physical Properties

The thermo-physical properties can be investigated by measuring glass transition temperature using differential thermal analysis.

5.2.5.1 Differential Thermal Analysis (DTA)

The glass transition temperature $T_g$ were measured by using differential thermal analysis (DTA) using platinum/alumina crucible. DTA thermogram of one of chalcohalide glasses SSCI-4 is as shown in Fig. 5.5. The glass transition temperature values are given in Table 5.2. Two characteristic phenomena are clear in the studied temperature region. The first distinct endothermic peak corresponding to the glass transition temperature $T_g$ located at about $167^\circ C$ and second, the crystallization exothermic peak $T_c$, which corresponds to the temperature of $220^\circ C$.

![DTA thermogram of the chalcohalide glass](image)

Fig. 5.5: DTA thermogram of the chalcohalide glass

5.2.6 Optical Properties

The optical properties especially in the infrared region were measured by FTIR and UV-Vis measurements.
5.2.6.1 Fourier Transform Infrared (FTIR) Analysis

The infrared transmittance spectra were recorded on a fourier transform infrared spectrometer in the frequency range of 200-4000 cm\(^{-1}\). FTIR spectra of SSCI-4 glass were as shown in Fig. 5.7. This composition has high transmission of 75% in the range 10-30\(\mu\)m which is in the acceptable range for an infrared application.

![FTIR spectra of 0.4Sb\(_2\)Se\(_3\)-0.6CuI glass](image)

Fig. 5.7: FTIR spectra of 0.4Sb\(_2\)Se\(_3\)-0.6CuI glass

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample Code</th>
<th>X (mol %)</th>
<th>Density (g/cc)</th>
<th>Mol. vol. (cc/mol)</th>
<th>DTA</th>
<th>Microhardness kg/mm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SSCI-2</td>
<td>60</td>
<td>5.50</td>
<td>66.26</td>
<td>156</td>
<td>108.2</td>
</tr>
<tr>
<td>2</td>
<td>SSCI-4</td>
<td>40</td>
<td>5.592</td>
<td>54.796</td>
<td>167</td>
<td>116.2</td>
</tr>
</tbody>
</table>

Table 5.2: Values of thermal and mechanical parameters for xSb\(_2\)Se\(_3\)-(100-x) CuI glass
5.2.6.2 UV-Vis NIR Measurements

UV-Vis transmission of the polished glass disc was measured on JASCO spectrophotometer in the range 200-2700nm. The graph of absorbance ($\alpha$) v/s $\lambda$ is as shown in Fig. 5.8. The optical gap, $E_g$, is determined by extrapolation of the straight-line portions of the $(\alpha h\nu)^{1/2}$ v/s ($h\nu$) graph as shown in Fig. 5.9. The values of $E_g$ are given in Table 5.2. All the measurements have been carried out at room temperature.

![Graph of absorbance v/s wavelength for SSCI-4](image1)

**Fig. 5.8:** Variation of absorbance v/s wavelength for SSCI-4

![Graph of $(\alpha h\nu)^{1/2}$ v/s $h\nu$ for SSCI-4](image2)

**Fig. 5.9:** Plot of $(\alpha h\nu)^{1/2}$ v/s $h\nu$ for SSCI-4
5.2.7 Field Emission Scanning Electron Microscopic Observations

Field emission scanning electron microscope was used for the investigation of surface morphology of the glass. The FESEM micrographs of the SSCI-2 and SSCI-4 glass are presented in Fig. 5.10 & Fig. 5.11. The FESEM images show how formation nano-strips of 100-150 nm in the glass matrix (Fig. 5.10) and nanoparticles of 50-100 nm (Fig. 5.11).

Fig. 5.10: FESEM image of SSCI-2

Fig. 5.11: FESEM image of SSCI-4
5.2.8 I-V Characteristics

The I-V characteristics of these samples were measured by using Keithley source meter (Model 2410) controlled by LabVIEW6i (National Instruments). The source-meter is capable of sourcing a constant current in the range 0-20 mA at a compliance voltage of 1100V (max). The glass samples polished to about 0.35 mm thickness were mounted in a special holder, between a point contact top electrode and a flat plate bottom. A constant current is passed through the sample and the voltage developed across it, is measured. The sample exhibited switching behaviour. The electrical switching characteristics of xSb_2Se_3-(1-x)CuI glasses are shown in Fig. 5.12, which indicates the compositional dependent switching behaviour. The composition with low as well a high CuI content shows switching behaviour. It may be noted that the threshold switching is reversible whereas memory switching is irreversible in both SSCI-2 & SSCI-4.

![Graphs showing I-V characteristics](image)

Fig. 5.12: Variation of Current I v/s Voltage V for sample (a) SSCI-2, (b) SSCI-4
The memory switching in chalcogenide glasses is known to involve crystallization of the material. The connectivity of the structural network of a chalcogenide glass has an important role in the crystallization of the material and consequently on the memory switching. If the network connectivity is high, the steric hindrances for structural reorganizations will be higher. Hence, the crystallization becomes more difficult and the material is less likely to show memory switching.

5.3 Results and Discussion

The thermo-physical and mechanical properties of chalcogenide and chalcocalcide glasses depend on the structural and energetic factors. The formation of structural units at the atomic scale is correlated with the bond energy and the preparation condition. The density measured at 20°C by Archimede’s method was found to be 5.59 gm/cc with an accuracy of +/-0.5%. The DTA thermogram for SSCI-4 sample is shown in Fig. 5.5. We observe from this graph that the glass transition temperature $T_g$ is at 167°C and the crystallization peak $T_c$, is at 220°C. The thermal stability of the glass samples has been described in terms of temperature difference between glass and crystalline state $i.e. (T_c-T_g)$. The higher value of about 50 reflects a good thermal stability. The glass transition temperature ($T_g$) appears to depend on the bond energy between the constituents. The $T_g$ also depends on the structure of glasses; it tends to increase with increasing dimensionality of glass structures. The connectivity of their atomic networks can be controlled since the glasses comprise electronegative chemical species with notably different binding characters. Hence, when an ionic halogen is added to a covalently bonded chalcogen-based network, it can form non-bridging structural motifs that reduce the network connectivity and glass transition (Mitkova and Boolchand,
Further, the high atomic-mass chalcogens and halogens bond with different kinds of metal or semimetal to form structures characterized by low phonon-like energies. The chalcohalide glasses, therefore, compete with pure chalcogen and pure halogen-based glasses in terms of their excellent infrared transmission and opportunity for optical devices operating in this wavelength range (Lucas, 2000). The recent theoretical and experimental investigations indicate that in several chalcogenide glassy systems, the rigidity percolation spans over a range of compositions (Selvanathan and Bresser *et al.*, 2000; Georgiev *et al.*, 2000; Micoulaut and Phillips, 2003; Micoulaut, 2006). These systems are characterized by three different phases namely, the floppy, the intermediate and rigid phases. There are two distinct transitions in such glasses, namely from the floppy to the isostatically rigid state and from the isostatically rigid to the stressed rigid state. Further, the compositions between the onset and completion of an extended stiffness transition are now commonly known as the thermally reversing window as the non-reversing enthalpy is found to nearly vanish for these compositions. In chalcohalide glasses, the thermally reversing window is generally found to be very sharp, restricted to a narrow composition range (Boolchand *et al.*, 2001; Pattanayak *et al.*, 2007). The differential thermal analysis studies reveal that there is a sharp thermally reversing window for SSCI-4. Halogens in covalent systems are monovalent, and possess a coordination number of one. Consequently, the addition of halogens to the chalcogenide glasses results in a disruption of their three-dimensional network, leading to interesting properties. This composition has high transmission of 75% in the range 10-30µm which is in the acceptable range for an infrared application. An FTIR spectrum for SSCI-4 is shown in Fig. 5.7. TEM and SEM have been used to prove the formation of nanosized particles. The FESEM
micrograph of the SSCI-2 and SSCI-4 glass is presented in Fig. 5.10 and Fig. 5.11. It shows nano-strips of 100-150 nm size in the glass matrix; some crystalline growth of nano phase has also been observed (Fig. 5.10). In some of the glasses the nanoparticles of 50-100 nm size were observed (Fig. 5.11).

We have further carried out neutron diffraction studies to understand the short range order and the network connectivity in this glass (Rashmi et al., 2012). The $S(Q)$ v/s Q is as shown in Fig. 5.3 and $T(r)$ v/s r is as shown in Fig. 5.4. In the total correlation graph, the peaks give us the positions of various interactions present in the system. From these peaks we can understand the short range order and network connectivity in this glass. The short range order mainly consists of Sb-Se bonds as well as Cu-Se bonds. Se-Se bonds are ruled out as the first 2 peaks in $T(r)$ are larger and match with Sb-Se and Cu-Se (also Cu-I) bonds. The distances are 2.48(1)Å and 2.66(1)Å. From the bond energy considerations these are more preferable bonds. The co-ordinations obtained are 2.9(2) and 3.7(2). The Cu-I bonds also are preferred and come around the same distances. If we assume one Cu-I bond then there are 3.0(2) Cu-Se bonds. Similarly Sb-I bonds also come around the identified Sb-Se distance. So if we assume that there is one Sb-I bond, then we will have 2.2(2) Sb-Se bonds. From these results we can say that Sb-(Se, I) pyramids are connected to Cu-(Se, I) bonds with co-ordinations of 3 and 4. We have further investigated the network connectivity for SSCI-4. Se-Se (non-bonding), Sb-Se ($2^{nd}$ neighbour) and Cu-Cu distances are identified to be in the r-range of 3.5Å to 4.2Å. Our results are in good agreement with the known distances in the chalcohalide glasses (Salmon and Shuqin Xin, 2002). Cu seems to be actively participating in the network formation. Further analysis is being carried out to understand the network connectivity. Usually, chalcogenide glasses are understood using continuously ordered chemically ordered network model (COCRN). In this model
stability of bonds is the guiding factor in determining the closest interactions. We found that short range order mainly consists of Sb-Se bonds as well as Cu-Se bonds. From the bond energy calculations these are the more preferred bonds. Thus, Cu seems to be actively participating in the network formation showing strong covalent nature. Since the composition SSCI-2 has higher amount of Sb₂Se₃ and it is prone to devitrification, the growth of nano-size strips/crystallites seems to be quite reasonable. The Cu supports nucleation of nanosized particles in glass matrix in this composition. The crystallites could be of Sb₂Se₃ which needs to be further investigated by HRTEM and high resolution XRD.

Fig. 5.12, that these samples (SSCI-2 & SSCI-4) exhibit a compositional dependent switching behaviour. The samples with high as well as low CuI content show memory switching behavior but seems to have dependence on composition as well as on microstructure. This can be understood on the basis of the sharp increase in the thermal diffusivity. Memory switching in chalcogenides is mostly a thermal process, which involves phase transformation from amorphous to crystalline state. During the process of switching Se atoms can easily move because of lesser atomic radii and also their bond angles can be easily deformed due to the higher compressibility. Hence, in Se-based glasses, the tendency toward regaining its initial state is less after deformation and as a result they always exhibit memory. In addition, FESEM studies exhibited the formation of nano-size strips/crystallites in 0.6Sb₂Se₃-0.4CuI. We find the switching behavior in this sample is different (somewhat diffused) from sharper switching for the sample having lower amount of Sb₂Se₃. We propose that role of Cu in network formation combined with the formation of nano-crystalline structure might be the cause of this type of switching in 0.6Sb₂Se₃-0.4CuI. However this need to be further investigated.
5.4 Conclusions

We obtained one of the compositions in the series (xSb$_2$Se$_3$(1-x)CuI, (x=1, 0.6, 0.5, 0.4, 0.3), with x=0.4 in glassy form by melt quenching under vacuum showing about 75% transmission in infrared range of 10-30µm. This shows its potential as glass for infrared application. It may be mentioned that glasses containing Cu have better resistance to cracks propagation and a higher hardness but are less stable against crystallization. We observed from FESEM measurements of chalcocohalide glass nanostrips of 100-150 nm in the glass matrix and some nanoparticles of 50-100 nm.

Further from neutron diffraction technique it was clear that short range order in SSCI-4 mainly consists of Sb-Se bonds as well as Cu-Se bonds. Se-Se bonds were ruled out as the first 2 peaks in T(r) were larger and matched with Sb-Se and Cu-Se (also Cu-I) bonds. The distances of these correlation were 2.48(1)Å and 2.66(1)Å. From these investigations we can say that Sb-(Se, I) pyramids are connected to Cu-(Se, I) bonds with co-ordinations of 3 and 4. Cu seems to be actively participating in the network formation. The bulk, melt-quenched xSb$_2$Se$_3$(1-x)CuI glasses have been found to exhibit memory switching behavior with low as well as high CuI content but seems to have a dependence on composition as well as on microstructure. During the process of switching Se atoms easily move because of lesser atomic radii (1.17 Å) and also their bond angles can be easily deformed due to the higher compressibility (11x10$^{-12}$ cm$^2$/dyn). Hence, in Se-based glasses, the tendency toward regaining its initial state is less after deformation and as a result they exhibit memory switching behaviour.