Chapter 6

FT-IR Studies of Impurities in In-Se-Tl Glasses

Summary

Chalcogenide glasses with composition $\text{In}_{10}\text{Se}_{90-x}\text{Tl}_x$ ($7 \leq x \leq 15$) and $\text{In}_{15}\text{Se}_{85-x}\text{Tl}_x$ ($2 \leq x \leq 10$) are synthesized by melt-quenching technique. The FT-IR transmission spectroscopy studies using KBr pellet method in the wavelength range of 400-4000 cm$^{-1}$ was carried out. The In-Se-Tl glasses studies show good transparency in the entire spectral range. There is an increase in percentage of transmittance values with increase in the Tl content. In the transmittance curve, various absorption bands are seen, which are related to chemical bonds of different extrinsic impurities present in the glassy material. The vibrational properties of the impurities in the powdered samples were measured. Vibrational modes attributed to O-H hydroxyl groups, molecular H$_2$O and carbon impurity atoms were detected in the mid-IR spectra.
6.1 Introduction

Chalcogenide glasses are disordered materials owing to transmit longer IR wavelengths (0.5-16µm). Stability against crystallization, chemical durability and their flexibility. The composition dependence of spectral transparency ranges for S/Se/Te based glasses are 0.5-7/0.8-12/1.2-16µm, respectively [1-3]. The selenium-based chalcogenide glasses have many active and passive applications in the field of memory switching devices, holographic recording systems, solar cells, thermal imaging systems and infrared sensors [4-6]. Chalcogenide glasses are cheaper than the crystalline substances; hence they are more attractive for device mass production. The application possibilities of chalcogenide glasses in IR optics are, most of the time, restricted by vibrational absorption bands of impurities, they are introduced during or after the glass synthesis [4], but these glasses have relatively high refractive index and intrinsic loss due to nano-voids, bubbles, pores and cracks. The contamination of chalcogenide glasses by carbon, oxygen, hydroxyl groups and some metals may remarkably increase the optical loss [7]. The only way to overcome this obstacle is by choosing proper glass compositions with minimal ability of covalent-bonded glass-forming network to chemical interaction with absorbed impurities. In this paper, the preparation and transmission loss characteristics of In_{10}Se_{90-x}Tlx (7 ≤ x ≤ 15) and In_{15}Se_{85-x}Tlx (2 ≤ x ≤ 10) chalcogenide glasses are presented.

6.2 Experimental

Bulk In_{10}Se_{90-x}Tlx (7 ≤ x ≤ 15) and In_{15}Se_{85-x}Tlx (2 ≤ x ≤ 10) glasses are prepared by vacuum-sealed melt-quenching method. The amorphous nature of the quenched sample is confirmed by the absence of sharp peak in the X-ray diffraction pattern. Some part of the prepared bulk glasses are ground to powdered. For IR measurements, the powdered glasses (~2mg) are mixed with spectroscopic grade KBr (200mg each) and the mixtures pressed into pellets and dried at 100ºC for one hour. The FT-IR measurements are performed at the ambient temperature in the spectral range of 400-4000cm\(^{-1}\) with the resolution of 1cm\(^{-1}\). It is supposed that changes in the intensity of impurity absorption bands correspond to the changes in the concentration of respective complexes incorporated into glass matrix, which is detected by spectral range of the apparatus used.
6.3 Results and Discussion

Figures 6.1 and 6.2 show infrared spectra of powdered In_{10}Se_{90-x}Tl_x (where x = 7, 9, 11, 13 and 15) and In_{15}Se_{85-x}Tl_x (where x = 2, 4, 6, 8 and 10) glassy systems, respectively. Generally, oxide and hydroxide impurities are present in chalcogenide glasses. The observed absorption bands are identified as vibrational bands of these impurity bonds. The position of the detected absorption bands are identified using experimental results [8-16].

![Image of IR transmission spectra](Image)

**Figure 6.1:** The IR transmission spectrum of In_{10}Se_{90-x}Tl_x (7 \leq x \leq 15) system

Both the series of studied glasses showed good transmittance in the entire mid-IR spectral range (400-4000 cm\(^{-1}\)). For all the samples of In_{10}Se_{90-x}Tl_x and In_{15}Se_{85-x}Tl_x chalcogenide glasses, the most intensive and broadest band appeared within the range of 3600-3800 cm\(^{-1}\) with a minimum centered around 3750 cm\(^{-1}\). This absorption band is associated with the vibrational modes of O-H hydroxyl groups bonded with external hydrogen or atoms of chalcogenide glassy structural network [9-11]. The other much
intense and sharpest band appeared around 1645 cm\(^{-1}\), associated with molecular adsorbed H\(_2\)O.

![IR transmission spectrum](image)

**Figure 6.2:** The IR transmission spectrum of In\(_{15}\)Se\(_{85}\)\(_-\)xTl\(_x\) (2 \(\leq\) x \(\leq\) 10) system

The reason for the appearance of these two absorption bands may be due to moisture absorbed by the sample from the surroundings during the sample synthesis and also during IR measurements.

The intensity of all absorption bands in In\(_{10}\)Se\(_{90}\)\(_-\)xTl\(_x\) (7 \(\leq\) x \(\leq\) 15) and In\(_{15}\)Se\(_{85}\)\(_-\)xTl\(_x\) (2 \(\leq\) x \(\leq\) 10) chalcogenide glasses mainly depend on their chemical composition and/or average coordination number \(<r>\) [16,17]. The chemical composition with corresponding \(<r>\) values and various positions of impurity bands are summarized in tables 6.1 and 6.2. For both the series, the indium contents are constant and hence, the observed variations in the intensity of these two bands are explained on the basis of Tl concentration. By increasing the Tl content, the metallic character of chemical bond increases, thus the probability of Tl atoms interacting with these impurities increases.
It is known that atomic compactness decreases with increasing average coordination number \( <r> \) for all chalcogenide glasses. The decrease in the compactness leads to the increase of free volume resulting in voids in the structural network [18] which is formed during melt-quenching process. The voids are responsible for the compositional dependence of various observed impurity bands.

Figure 6.3 shows the variation of percentage of transmittance with respect to the thallium content for both the series. From figure 6.3, it is revealed that there is an increase in the percentage of transmittance with increase in thallium content. It is known that the IR transmittance in chalcogenide glasses is mainly controlled by two factors, i.e., the reflectance of the surface and the absorption of the bulk materials. In the present study, the transmittance in both the series is found to increase almost linearly as the thallium content is increased. This is due to decrease in \( \text{H}_2\text{O} \) and \( \text{OH} \) absorption peak-width and intensity and also metallic factor of thallium. In the compositional transmittance spectrum, reduction in intensity and shift of the adsorbed \( \text{H}_2\text{O} \) and absorbed \( \text{OH} \) bands are observed. It is due to the fact that the Se tetrahedral bond stretching and Se\(_8\) chain bending modes, respectively [19-22].

<table>
<thead>
<tr>
<th>Vibrational modes</th>
<th>Vibrational band position (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{In}<em>{15}\text{Se}</em>{85-x}\text{Tl}_x , (2 \leq x \leq 10) )</td>
</tr>
<tr>
<td>( \nu_{\text{O}-\text{H}} )</td>
<td>Tl(_2) 3471 Tl(_4) 3480 Tl(_6) 3479 Tl(<em>8) 3489 Tl(</em>{10}) 3479</td>
</tr>
<tr>
<td>( \nu_{\text{C}-\text{H}} )</td>
<td>2917 2930 2926 2930 2925</td>
</tr>
<tr>
<td>( \nu_{\text{C}-\text{O}}, \nu_{\text{C}-\text{H}} )</td>
<td>2027 2037 -- 2080 2098</td>
</tr>
<tr>
<td>( \nu_{\text{H}-\text{O}}, \nu_{\text{O}-\text{H}} )</td>
<td>1662 1663 1663 1661 1655</td>
</tr>
<tr>
<td>( \nu_{\text{H}-\text{O}}, \nu_{\text{C}-\text{H}} )</td>
<td>1585 1582 1584 1587 1541</td>
</tr>
<tr>
<td>( \nu_{\text{C}-\text{O}} )</td>
<td>1063 1054 1072 1066 1069</td>
</tr>
</tbody>
</table>

**Table 6.1:** Positions of impurity bands in the IR spectra of powdered \( \text{In}_{15}\text{Se}_{85-x}\text{Tl}_x \) glasses

The oxide impurities are strongly dependent on the chemical composition of chalcogenide glasses. In mid/near/far IR spectra, absorption bands are present in relation to vibration of oxygen atoms bonded to basic elements and/or to carbon impurities atoms. A band observed in the spectral range of 700-800cm\(^{-1}\) for
In$_{15}$Se$_{85-x}$Tlx (2 $\leq$ x $\leq$ 10) glasses assigned to phonon absorption of In-O bonds in the powders.

<table>
<thead>
<tr>
<th>Vibrational modes</th>
<th>Vibrational band position (cm$^{-1}$)</th>
<th>In$<em>{10}$Se$</em>{90-x}$Tlx (7 $\leq$ x $\leq$ 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tl$_7$</td>
<td>Tl$_9$</td>
</tr>
<tr>
<td>VO-H</td>
<td>3743</td>
<td>3744</td>
</tr>
<tr>
<td>VC-H</td>
<td>2930</td>
<td>2930</td>
</tr>
<tr>
<td>VC-O-Se</td>
<td>2068</td>
<td>2093</td>
</tr>
<tr>
<td>VO-H</td>
<td>1698</td>
<td>1699</td>
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<tr>
<td>VH-O-H</td>
<td>1522</td>
<td>1525</td>
</tr>
<tr>
<td>VC-O; VC-H</td>
<td>1049</td>
<td>1061</td>
</tr>
</tbody>
</table>

Table 6.2: Positions of impurity bands in the IR spectra of powdered In$_{10}$Se$_{90-x}$Tlx glasses.

Figure 6.3: The variation of percentage of transmittance with thallium content of In$_{10}$Se$_{90-x}$Tlx and In$_{15}$Se$_{85-x}$Tlx glassy systems.

The broad and asymmetric band centered between 550 and 675 cm$^{-1}$ is attributed to vibrational mode of Tl-O bonds. The content of molecular adsorbed water is broad.
and asymmetrical band due to higher degree of metallization in chemical bonds of Tl atoms that interact with impurities. All other absorption bands detected in the IR spectra are very weak and are not dependent on the glass composition. They are assigned to vibrations of carbon impurities in different configurations. The absorption bands in the range of 2917-2930 cm\(^{-1}\) and 1045-1072 cm\(^{-1}\) are assigned to stretching and bending vibration of C-H bonds, respectively, in CH\(_2\) and/or CH\(_3\) impurity groups [10,19]. The broad and very weak band centered at \(\approx 2080\) cm\(^{-1}\) is assigned to C-O-Se impurity groups due to contamination of the raw materials [10,12]. On summarizing, it is shown that the influence of O- and C-containing complexes on the IR transmittance spectra is insignificant in comparison with that of water-related impurities.

### 6.4 Conclusion

Extrinsic impurities in the powdered glassy alloys of In\(_{10}\)Se\(_{90-x}\)Tl\(_x\) (7 ≤ x ≤ 15) and In\(_{15}\)Se\(_{85-x}\)Tl\(_x\) (2 ≤ x ≤ 10) are studied by FT-IR spectroscopy in 4000-400 cm\(^{-1}\) region. From the transmittance spectra curve, it is revealed that the water related impurities, which are dominant over the impurities of O- and C-containing bands. It shows that Se-enriched glasses can be used in 4000-3700 and 3200-1700 cm\(^{-1}\) IR regions.
References