IR Studies of Impurities in In-Se-Tl Bulk Chalcogenide Glassy System

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ABSTRACT

Chalcogenide glasses with composition $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) and $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) are synthesized by melt quenching technique. The FT-IR transmission spectroscopy studies using KBr pellet method in the wavelength range 400-4000 cm^{-1} has been carried out. The In-Se-Tl glasses studies shows 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 are measured. Vibrational modes attributed to O-H hydroxyl groups, molecular H_2O and carbon impurity atoms were detected in the mid-IR spectra.

Keywords - Chalcogenide glasses, FTIR, XRD and **Thallium addition.**

I. INTRODUCTION

Chalcogenide glasses are disordered materials owing to transmit longer IR wavelengths (0.5-16 μm), Stability against crystallization, chemical durability and their flexibility. The composition dependence of spectral transparency ranges for S/Se/Te based glasses are 0.5-7/0.8-12/1.2-16 μm 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 being introduced during or after the glass synthesis [4], but these glasses have relatively high refractive index and intrinsic loss due to nanovoids, 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 $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) and $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) chalcogenide glasses are presented.

II. Experimental details

Bulk $In_{10}Se_{90-x}Tl_x$ ($7 \leq x \leq 15$) and $In_{15}Se_{85-x}Tl_x$ ($2 \leq x \leq 10$) glasses have been prepared by vacuum sealed melt quenching method. High purity (99.99%) In, Se and Tl in appropriate atomic percent proportions are weighed using an electronic balance and are sealed in quartz ampoules (length ~ 5 cm and inner diameter ~ 8 mm) under the vacuum of 10^{-5} Torr in order to avoid the reaction of glasses with oxygen at higher temperature. The sealed quartz ampoule containing sample is loaded in a horizontal rotary furnace and heated up to 850 ℃ at the rate of 100-120 ^{0}C/ hour and rotated at 10 rpm continuously for about 36 hour to ensure a high degree of homogeneity of the melt. Quenching has been done subsequently in ice water + NaOH mixture. The ingots of the samples are taken out by breaking the quartz ampoules. The amorphous nature of the quenched sample is confirmed by the absence of sharp peak in the X-ray diffraction pattern. After preparation, part of the bulk glasses are powdered. For IR measurements, the powdered glasses (~2 mg) are mixed with spectroscopic grade KBr (200 mg each) and the mixtures pressed into pellets and dried at 100 ^{0}C for one hour. The FTIR measurements are performed at the ambient temperature in the spectral range of 400-4000 cm^{-1} with the resolution 1 cm^{-1}. It is supposed that changes in the intensity of impurity absorption bands corresponds to the changes in the concentration of respective complexes incorporated into glass matrix which is detected by spectral range of the apparatus used.

III. Results and Discussion

Figure (1) and (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 may be present in chalcogenide glasses. The observed absorption bands are identified as vibrational bands of these impurity bonds. The position of the detected

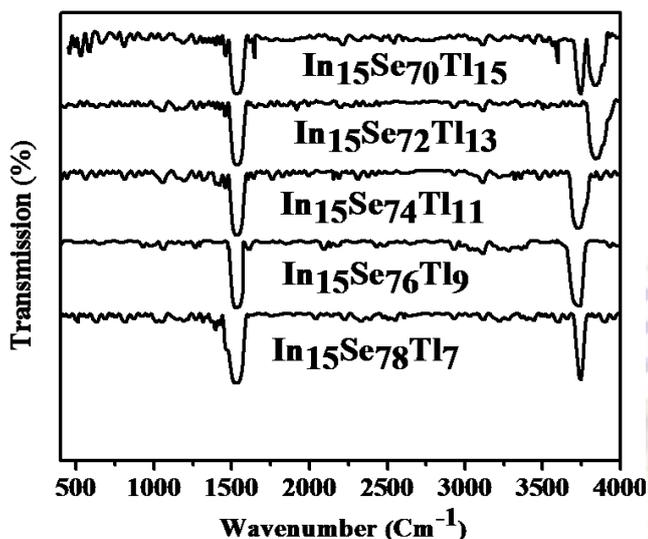absorption bands are identified using previous experimental results [8-16].

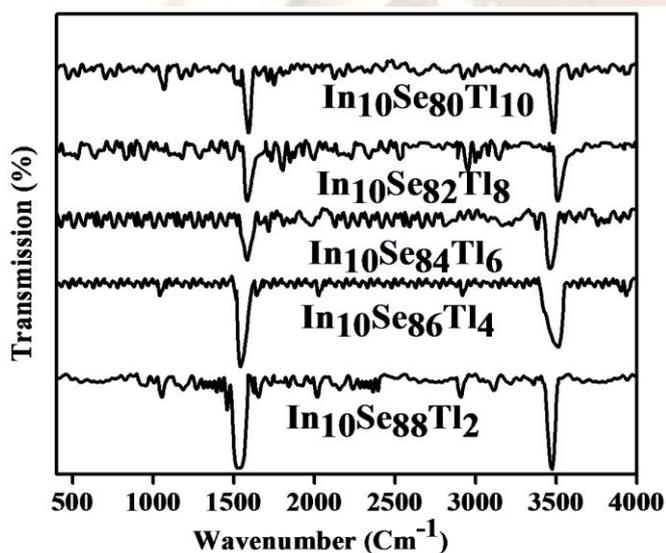Figure 1: The IR transmission spectrum of $In_{10}Se_{90-x}Tl_x$ (where x=7,9,11,13 and 15) System.

Figure 2: The IR transmission spectrum of $In_{15}Se_{85-x}Tl_x$ (where x=2,4,6,8 and 10) System.

Both the series of studied glasses showed good transmittance in the entire mid IR spectral range (400-4000 cm^{-1}). For all the five 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 can be 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_2O. 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 $In_{10}Se_{90-x}Tl_x$ (7≤x≤15) and $In_{15}Se_{85-x}Tl_x$ (2≤x≤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 TABLE 1. For both the series, the indium contents are constant and hence, the variation observed in the intensity of these two bands can be 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 decreasing of the compactness leads to the increasing of free volume resulting in voids in the structural network [18] which may be formed during melt quenching process. The voids are responsible for the compositional dependence of various observed impurity bands.

Fig. 3 shows the variation of percentage of transmittance with respect to the thallium content for both the series. From fig. 3, it is revealed that there is an increase in 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 H_2O and OH absorption peak-width and intensity and also metallic factor of thallium. In the compositional transmittance spectrum, reductions in intensity and shift of the adsorbed H_2O and absorbed OH bands have been observed. It may be due to the fact that the Se tetrahedral bond stretching and Se_8 chain bending modes respectively [19-22].

The oxide impurities are strongly dependent on the chemical composition of chalcogenide glasses. In Mid/Near/Far IR spectra, absorption bands are present related to vibration of oxygen atoms bonded to basic elements and/or to carbon impurities atoms. A band observed in the spectra range 700-800 cm^{-1} for $In_{15}Se_{85-x}Tl_x$ (2≤x≤10) glasses assigned to phonon absorption of In-O bonds in the powders. The broad and asymmetric band centered between 550-675 cm^{-1} can be attributed to vibrational mode of Tl-O bonds.

The content of molecular adsorbed water broad and asymmetrical band due to higher degree of metallization of chemical bonds of Tl atoms are interact with impurities.

Vibrational modes	Vibrational band position (cm^{-1}) In$_{15}$Se$_{85-x}$Tl$_x$ (2≤x≤10)					Vibrational band position (cm^{-1}) In$_{10}$Se$_{90-x}$Tl$_x$ (7≤x≤15)				
	Tl$_2$	Tl$_4$	Tl$_6$	Tl$_8$	Tl$_{10}$	Tl$_7$	Tl$_9$	Tl$_{11}$	Tl$_{13}$	Tl$_{15}$
ν_{O-H}	3471	3480	3479	3489	3479	3743	3744	3743	3743	3750
ν_{C-H}	2917	2930	2926	2930	2925	2930	2930	2930	2928	2927
ν_{C-O-Se}	2027	2037	--	2080	2098	2068	2093	2089	2019	2093
ν_{O-H}	1662	1663	1663	1661	1655	1698	1699	1697	1697	1698
ν_{H-O-H}	1585	1582	1584	1587	1541	1522	1525	1530	1537	1545
ν_{C-O}; ν_{C-H}	1063	1054	1072	1066	1069	1049	1061	1057	1049	1055

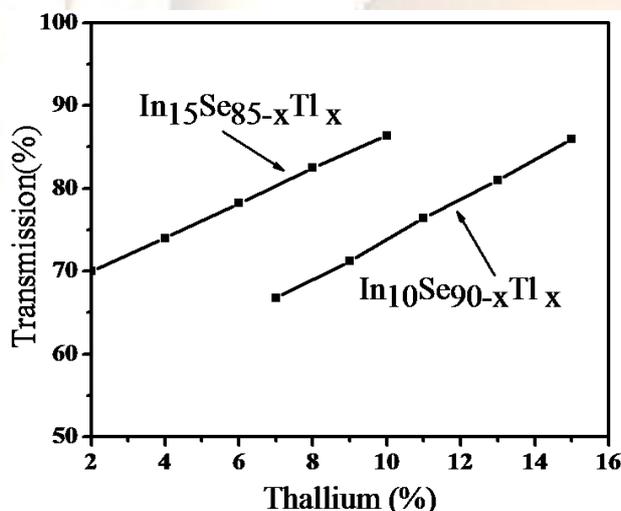Table 1: Position of impurity bands in the IR spectra of powdered In-Se-Tl glasses.

Figure 3: The variation of percentage of transmittance with thallium content of In$_{10}$Se$_{90-x}$Tl$_x$ and In$_{15}$Se$_{85-x}$Tl$_x$ glassy systems.

All other absorption bands detected in the IR spectra are very weak and do not dependent on the glass composition. They can be assigned to vibrations of carbon impurities in different configurations. The absorption bands in the range 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 ~ 2080 cm-1 has been assigned to C-O-Se impurity groups due to contamination of the raw materials [10, 12]. 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.

IV. 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.

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