



RAMAN AND IR STUDIES ON TELLURITE BASED LITHIUM SELENITE GLASSES

P. SATYA GOPAL RAO¹, RAJESH SIRIPURAM² AND SURESH SRIPADA^{3*}

^{1,2,3} Department of Physics, JNTUHCEJ, Nachupally, Karimnagar, Telangana, India.

*Corresponding Author e-mail: sripada_suresh2020@rediffmail.com

ABSTRACT

Raman and IR studies of TeO₂-SeO₂-Li₂O ternary glass system have been investigated for structural evaluation. All glass samples were prepared by conventional melt quenching method. The amorphous nature was confirmed by X-Ray Diffraction technique. The Raman frequencies are observed at 350 cm⁻¹, 461-453 cm⁻¹, 665-661 cm⁻¹ and 780-751 cm⁻¹ and they are assigned with references. The IR frequencies 561 cm⁻¹, 796-770 cm⁻¹ and 1094-1145 cm⁻¹ are observed. From both the techniques, the main building blocks TeO₃, TeO₄, LiO₄ and SeO₃ were determined and structural modification is taken place in present glass system with change of Li₂O composition and as well as TeO₂ composition. It is observed that TeO₄ units are converted to TeO₃ units which are interconnected with the selenium units. Comparison study is done in between TeO₂ of 90 mol % and TeO₂ of 80 mol% for present study. Addition of Li₂O to selenium tellurite glass, there is increases in TeO₃ tp with NBOs which are build up the glassy network.

Key words: Raman spectra, IR spectra, tellurite based glasses, selenite-tellurite glasses.

1. INTRODUCTION

The Tellurium dioxide based glasses have very wide glass forming range and useful properties such as low melting temperature, high linear and non-linear refractive indices, high transmission, low melting point and easy fabrication and good transmittance of infrared. Because of these peculiar characteristics, Tellurite glasses are excellent materials for applications in non-linear optics and optical waveguides [1, 2]. In addition to these, Tellurite glasses are scientifically and technologically important materials for their high Raman gain coefficients, transmission capability, high chemical durability, low glass transition temperature [3]. Selenite glasses having tremendous potential applications such as super-ionic semiconductors, non-linear optical devices, sensors, solar cells, photocells and reflecting windows etc. [4-10]. When Tellurite combine with selenite as second component of glass-forming oxides [11, 12] it decreases the melting temperature of glass compositions and change their optical properties [13-16]. Because of these tremendous applications from individual families of Tellurium and selenium based oxide glasses, it made us to investigate tellurium- selenium based glasses. Addition of Li₂O in tellurium- selenium glass system could improve the spectroscopic and physical properties the glasses. And also in TeO₂ based glasses it increases their glass forming tendency and produces non-bridging oxygen (NBO) sites which decreases the average coordination number, thus resulting in resistant to crystallization [17, 18]. The purpose of this paper is to obtain the structural evolution of 80TeO₂+ (20-x) SeO₂ + xLi₂O (where x=10, 15, 20) and 90TeO₂+ (10-x) SeO₂ + xLi₂O (Where x=5, 10) glass system by Raman, infrared spectroscopy and comparative study is done in between TeO₂ of 90 mol % and TeO₂ of 80 mol%.

2. Experiment Techniques

80TeO₂+ (20-x) SeO₂ + xLi₂O (Where x=10, 15, 20) and 90TeO₂+ (10-x) SeO₂ + xLi₂O (Where x=5, 10) glasses were prepared by melt quenching technique using 99.9% purity-grade oxides (Aldrich). The materials were well mixed in appropriate proportions to form 5g batches. The mixed proportions grounded in a mortar

with pestle for 30min to get homogeneity. Each batch was melted at 800 °C for 30 min in porcelain crucible in electric furnace to get bubble free liquid. The melt was then quenched rapidly between thick stainless steel plate which is pre-heated 200°C to avoid excess thermal shocks. The glasses were annealed for 4h at 200°C to relieve from mechanical strains. The composition of the two glass series and their sample codes are shown in Table 1. The amorphous nature of the glass at room temperature was determined by X-Ray diffraction pattern for the glasses (XRD- BRUKER D8 ADVANCE). Glasses were recorded to obtain infrared spectra (IR- BRUKER VECTOR22) in the range from 4000 to 400cm⁻¹ at room temperature. The high temperature Raman spectrometer (RAMAN- HORIBA JOBIN YOUN, MODEL- LABRAM 633nm laser wavelength) is used to find out its structural behavior at room temperature

Table 1 : Glass compositions and sample codes of 80TeO₂+ (20-x) SeO₂ +xLi₂O (Where x=10, 15, 20) and 90TeO₂+ (10-x) SeO₂ +xLi₂O (Where x=5, 10) glass system.

Glass code	Composition (mol %)
IITSL3	80TeO ₂ +10SeO ₂ + 10Li ₂ O
IITSL4	80TeO ₂ + 5SeO ₂ + 15Li ₂ O
IITSL5	80TeO ₂ + 20Li ₂ O
IIITSL2	90TeO ₂ + 5SeO ₂ +5Li ₂ O
IIITSL3	90TeO ₂ +10Li ₂ O

Table 2: Raman peak frequencies 80TeO₂+ (20-x) SeO₂ +xLi₂O (Where x=10, 15, 20) and 90TeO₂+ (10-x) SeO₂ +xLi₂O (Where x=5, 10) glass system.

Glass code	Peak frequencies (cm ⁻¹)			
IITSL3	350	461	665	780
IITSL4	350	461	665	780
IITSL5	350	461	665	751
IIITSL2	-	453	661	780
IIITSL3	-	453	661	780

Table 3 : Assignments of Raman bands of 80TeO₂+ (20-x) SeO₂ +xLi₂O (Where x=10, 15, 20) and 90TeO₂+ (10-x) SeO₂ +xLi₂O (Where x=5, 10) glass system.

Peak frequencies (cm ⁻¹)	Peak assignments
461-453	Bending vibrations of Te-O-Te or Te-O-Se linkages
665-661	Stretching vibrations of TeO ₄ trigonal bipyramid (tbp) units with NBO. Bending mode of Te-O-Te or O-Te-O linkages.
780-751	TeO ₄ (tbp) and stretching vibration of Tellurium and NBOs, TeO ₃₊₁ polyhedra or TeO ₃ trigonal pyramid (tp) units.
350	symmetric bending ν ₄ of TeO ₄ groups

Table 4 : Infrared absorption bands $80\text{TeO}_2 + (20-x) \text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=10, 15, 20$) and $90\text{TeO}_2 + (10-x) \text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=5, 10$) glass system.

Glass code			
IITSL3	624	770	1094
IITSL4	624	770	1145
IITSL5	624	770	1145
IIITSL2	652	770	1102
IIITSL3	561	796	1102

Table 5: Assignments of IR absorptions bands of $80\text{TeO}_2 + (20-x) \text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=10, 15, 20$) and $90\text{TeO}_2 + (10-x) \text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=5, 10$) glass system

Peak frequencies cm^{-1}	absorptions bands
561	Te-O bond vibrations, where the oxygen anions are considered non-bridging (NBO)
624	Stretching vibrations of Te-O bonding the TeO_4 and TeO_3 groups
652	Bonding mode of Te-O-Te or O-Te-O linkages the stretching mode TeO_4 tp with BO
770	stretching vibration of TeO_3 tp or TeO_{3+1} units
796	Stretching vibrations of Te-O bonds in the TeO_4
1094-1145	TeO_4 groups

3. RESULTS AND DISCUSSION

XRD and Raman Spectra

The X-ray diffraction patterns of all the glasses are shown in the Fig 1. From the Fig 1. No sharp peak has been observed, that confirms amorphous nature. The Raman spectra of the present glass system doped with alkali oxides reveals those different absorptions bands as shown in Fig.2, 3 respectively. The absorption bands are observed around 780-751, 665-661, 461-453, 350 and 34-64 cm^{-1} as shown in Table 2. The peak assignment are shown in Table 3. By adding alkali oxides to the present glasses the bands are affected around 780-751 cm^{-1} in the glass code II series. It is seen that in the II series glasses the band around 350, 461, 665 cm^{-1} does not change by changing the mol% concentration of SeO_2 and Li_2O . In the III series the bands 453, 661 and 780 cm^{-1} does not change by changing the mol% concentration of SeO_2 and Li_2O . The peak which is at 780-751

cm^{-1} is assigned to TeO_4 (tbp) and stretching vibration of Tellurium and NBOs, TeO_{3+1} polyhedra or TeO_3 trigonal pyramid (tp) units. The absorption bands $665\text{-}661\text{ cm}^{-1}$ is assigned to stretching vibrations of TeO_4 trigonal bipyramid (tbp) units with NBO sharing with bending mode of Te-O-Te or O-Te-O linkages [19-25], while at $461\text{-}453\text{ cm}^{-1}$ is assigned to bending vibrations of Se-O-Se and Te-O-Te or Te-O-Se linkages [26-28]. The absorption band 350 cm^{-1} at low frequency one is assigned to the symmetric bending ν_4 of TeO_4 groups [29]. The very weak peak which is at between $38\text{-}42\text{ cm}^{-1}$ and strong peak with a high intensity around $58\text{-}62\text{ cm}^{-1}$ is identified with the boson peak which is characteristic feature of a vitreous state. Although so many attempts made to explain the origin boson peak, generally it is related to long-range spatial correlations in the structure. It might be assigned as a boson peak associated to light scattering due to acoustic-like vibrations of the disordered structure [30-32]. The shoulders at frequency around 780 cm^{-1} for glasses IITSL3 and IITSL4 is same even though SeO_2 and Li_2O mol% changes but when Li_2O at 20 mol% the shoulder decreases to lower frequency side at 751 cm^{-1} that means the TeO_4 trigonal bipyramids to TeO_3 trigonal pyramids via intermediate types TeO_{3+1} polyhedra or TeO_3 trigonal pyramid (tp) units, simultaneously with an increase in the amount of NBO's. When alkali oxides concentration increases, it is found to increase in NBO's which indicates that Li_2O play a important role in modification of the present glass system. The comparison between 90 and 80 mol% TeO_2 , in the 80 mol% TeO_2 the boson peaks and one low frequency band are observed. The peak frequency bands 80 mol% TeO_2 are higher side when it is compare with 90 mol% TeO_2 , since the intensity of the Raman peak is proportional to the number of scattering units and their scattering efficiency. So TeO_2 is related to the creation of additional disorder in the TeO_2 chains involving other structural unit in them.

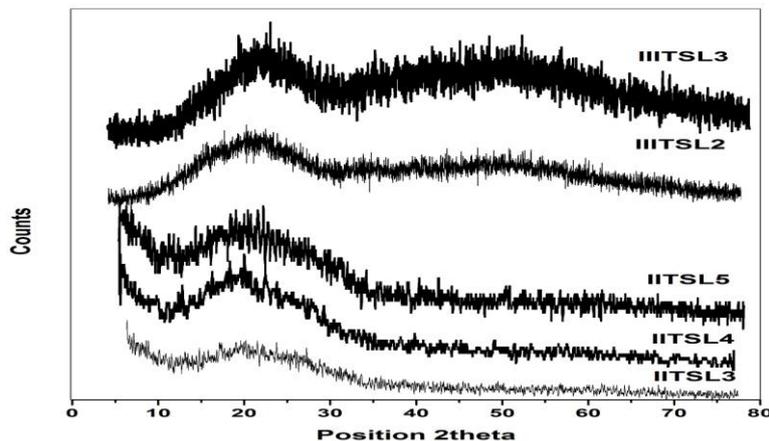


Fig1. X-ray diffraction pattern of $80\text{TeO}_2 + (20-x)\text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=10, 15, 20$) and $90\text{TeO}_2 + (10-x)\text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=5, 10$) glass.

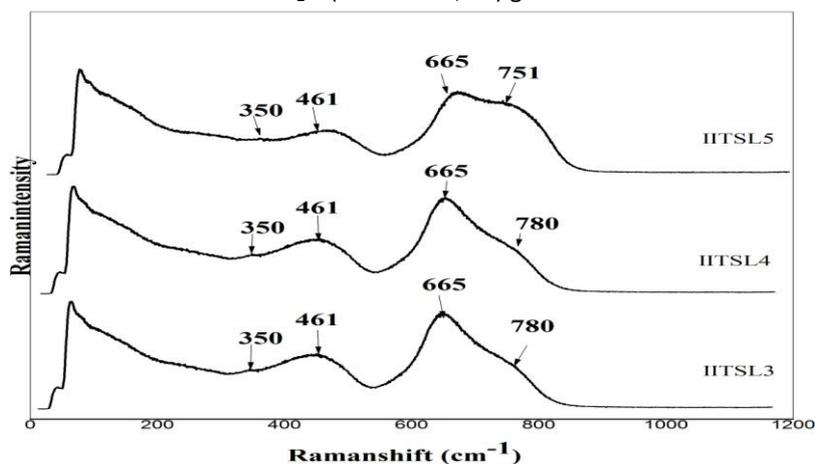


Fig 2. Raman spectra of $80\text{TeO}_2 + (20-x)\text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=10, 15, 20$) glass

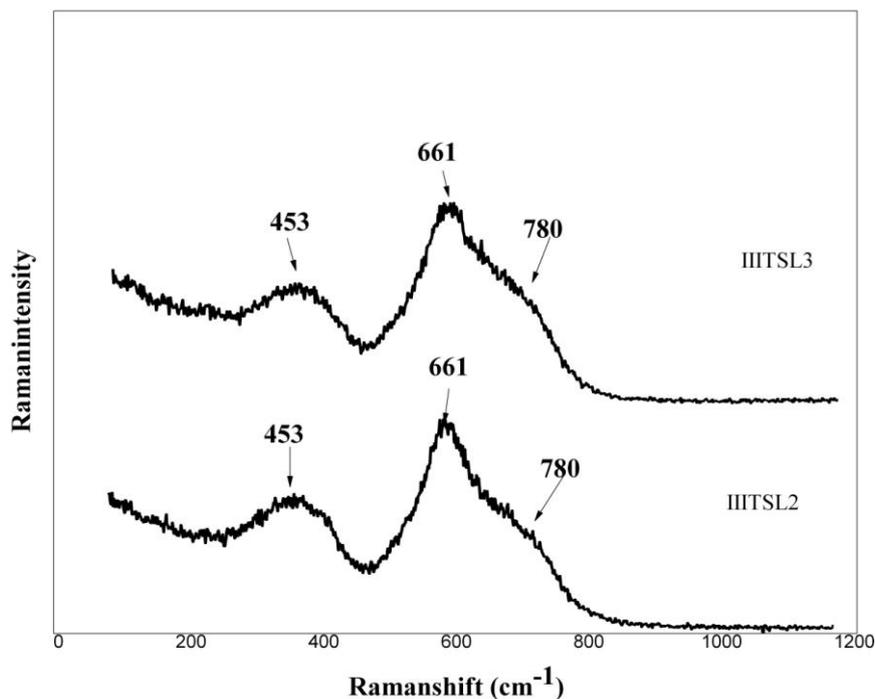


Fig 3. Raman spectra of $90\text{TeO}_2 + (10-x)\text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=5, 10$) glass.

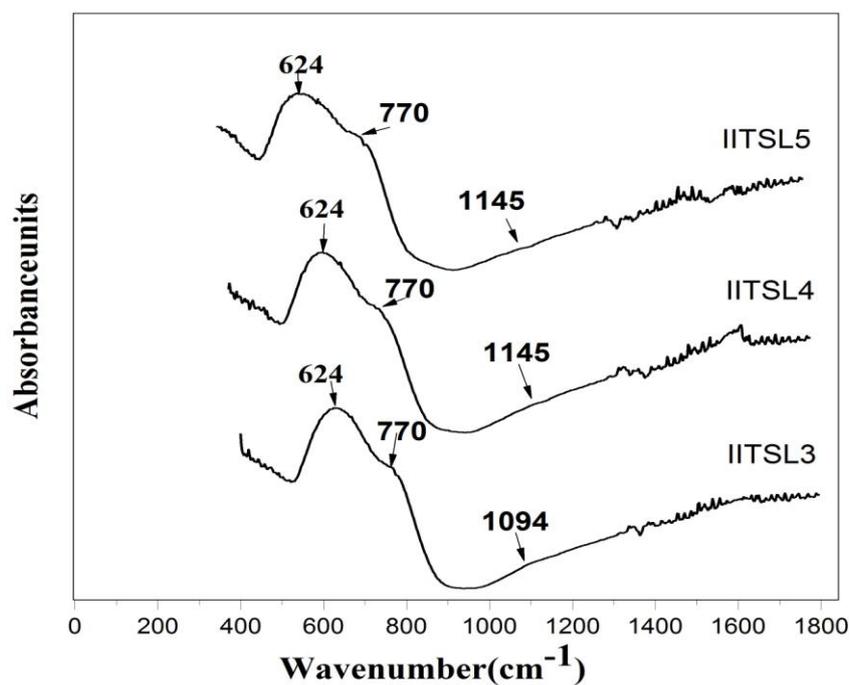


Fig 4. IR spectra of $80\text{TeO}_2 + (20-x)\text{SeO}_2 + x\text{Li}_2\text{O}$ (Where $x=10, 15, 20$) glass

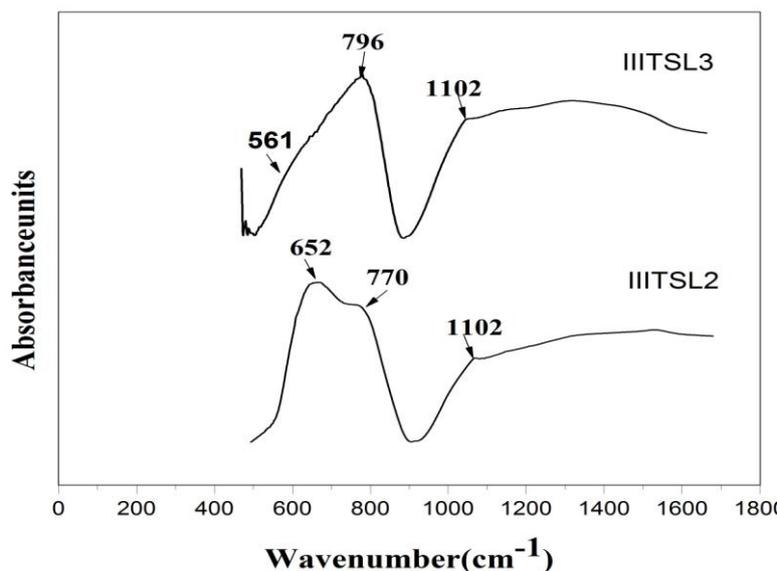


Fig 5. IR spectra of 90TeO₂+ (10-x) SeO₂ +xLi₂O (Where x=5, 10) glass.

IR spectra

The IR absorption spectra for various glass sample in the 80TeO₂+ (20-x) SeO₂ +xLi₂O (where x=10, 15, 20) and 90TeO₂+ (10-x) SeO₂ +xLi₂O (Where x=5, 10) glass system were recorded in the frequency region 1800-400 cm⁻¹ are shown in the Fig 4, 5 respectively. The observed absorption peaks frequencies and their assignments is shown in the table 4, 5 respectively. The main absorption peaks observed in the present glass system are 1094-1138 cm⁻¹, 796-770 cm⁻¹, 624 cm⁻¹ and 561 cm⁻¹. It is observed that in the II series glasses the band around 624,770 cm⁻¹ does not changed by changing the mol% concentration of SeO₂ and Li₂O .The shoulder around 561 cm⁻¹ in IIITSL3 glass is assigned to Te-O bond vibrations, where the oxygen anions are considered non-bridging (NBO)[33].The band 624 cm⁻¹ is attributed to Stretching vibrations of Te-O bonding the TeO₄ and TeO₃ groups[34], while at 652 cm⁻¹ band is assigned to bonding mode of Te-O-Te or O-Te-O linkages the stretching mode TeO₄ tp with BO[35].The shoulder 770 cm⁻¹ is assigned stretching vibration of TeO₃ tp or TeO₃₊₁ units[36].The intense absorption at 796 cm⁻¹ in IIITSL3 glass can be assigned to stretching vibrations of Te-O bonds in the TeO₄ units [37-39] .The bands between 1094-1145 cm⁻¹ is assigned to TeO₄ groups [35]. According to FTIR analysis of present glass system with the substitution SeO₂+Li₂O into TeO₂ glasses, the intensity peaks of the stretching vibrations of Te-O-Te or Te-O-Se linkages in TeO₄ units decreases which results in modification of network connectivity as shown in Fig 4,5 .This glass system also results in decrease in intensities of TeO₄ units and increase in the TeO₃₊₁ polyhedra or TeO₃ trigonal pyramid (tp) units due to the conversion of TeO₄ trigonal bipyramids to TeO₃₊₁ polyhedra or TeO₃ trigonal pyramid (tp) units. In the studied glass system it is concluded that with increase of Li₂O mol% at constant TeO₂ the TeO₄ tbp units decrease and peak related to TeO₃/ TeO₃₊₁ units increased. The comparison between 90 and 80 mol% TeO₂ in FT-IR spectra the absorption peaks around 1094-1145 cm⁻¹ are due to TeO₄ groups .It is observed from the Fig4, 5 the higher wave number absorption peak around 1094-1102 cm⁻¹ shifts to lower wave number side around 624,652,770 and 796 cm⁻¹ that is indication of transformation of TeO₄ units into TeO₃ units in the composition range 90 and 80 mol% of TeO₂ respectively. It is also clearly observed that absorption peak increases from 1094 to 1102 cm⁻¹ when TeO₂ mol% concentration increases from 80% to 90% due to increase in TeO₄ groups.

4. Conclusions

The structural evolution of the prepared glass samples was investigated by FT-IR absorption and Raman scattering. Characteristic units for tellurium [TeO₄ tbp, TeO₃₊₁ polyhedra and TeO₃ tp] were detected in the structure using FT-IR and Raman spectroscopic techniques. In the present glass system with Li₂O addition the coordination of TeO₂ leads to a gradual reduction of the tellurium coordination from TeO₄ →TeO₃₊₁ →

TeO₃ and substantial change of glass structure in accordance with another glass former role played by SeO₂, simultaneously with an increase in the amount of non-bridging oxygen. From the changes induced by lithium oxide in the glass structure can be concluded that it acts as a modifier in the studied samples. Glass compositions between 90 and 80 mol% TeO₂ is related to the creation of additional disorder in the TeO₂ network involving other structural units and this confirmed by both FT-IR and Raman data.

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