

Structural evaluation on $\text{TeO}_2\text{-SeO}_2\text{-R}_2\text{O}$ ternary glass system using Raman and IR

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Structural evaluation on $70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$ (R = potassium (K), sodium (Na) and lithium (Li)) ternary glass system has been studied using infrared (IR) and Raman techniques. Main building units of both glass formers (tellurium dioxide (TeO_2) and selenium dioxide (SeO_2)) play a vital role in the construction of amorphous network. According to the IR and Raman data, it is clear that the structural building units appearing in the glass system are selenium trioxide (SeO_3), lithium tetraoxide (LiO_4), potassium tetraoxide (KO_4), sodium oxide (NaO), tellurium trioxide (TeO_3) and tellurium tetraoxide (TeO_4). Adding alkali oxide to tellurium dioxide leads to a gradual reduction of the tellurium coordination from $\text{TeO}_4 \rightarrow \text{TeO}_{3+1} \rightarrow \text{TeO}_3$; in addition to this, selenium dioxide also plays vital role in forming the glass structure. Mixing potassium, sodium and lithium to the selenium–tellurite glass system results in cleavage of Te–O–Te and Se–O–Se linkages by formation of TeO_3^- and SeO_3^- terminal groups. Among these, tellurium trioxide units are the dominant basic structural entities. Glass structural fragments are associated with the type of alkali oxide (potassium, sodium and lithium) and sterical hindrance of heavy alkali oxide produces distortions of the glassy network and reduces its rigidity.

1. Introduction

Tellurite glasses are technologically important since they are chemically stable, have high homogeneity and are resistant to diversification at low temperatures ($T_g \approx 300^\circ\text{C}$). Apart from these properties, they have high refractive indices, high dielectric constant, good infrared (IR) transmission coefficients, high thermal expansion coefficients and so on. It has been demonstrated that the tellurite glasses are one of the promising materials for non-linear optical devices due to their large third-order non-linear susceptibility.^{1–5} These glasses exhibit electrical behavior as semiconductors and show electronic switching effects, which make them useful in electronic industry.⁶ Some tellurite glasses are also suitable for setting up optical fiber amplifiers.⁷ Because of their special optical properties, these materials are important for potential applications in laser technology and optical communication systems.^{8–11} Selenite glasses are of scientific and technological interest due to their ability to decrease the melting temperature of glass (for several compositions) and to change their optical properties.^{12–15} Selenite glasses have a number of applications such as super-ionic semiconductors, non-linear optical devices, sensors, solar cells, photocells and reflecting windows.^{16–22} On the other hand, tellurite combined with selenite as the second component of glass-forming oxides^{23,24} is new and this exotic class of non-traditional glasses have not been studied

much extensively till now. Because of the specific characteristics of individual families of tellurite and selenite glasses and their applications in various fields, researchers are paying much attention to the combination of both the glass formers. Investigation is in progress on selenite tellurite glasses by studying the spectroscopic and transport properties. The large number of applications of these glasses has led the authors to investigate their properties. In this glass system, they add small amounts of alkali group elements such as potassium (K), sodium (Na) and lithium (Li) as network modifiers, which results in cleavage of the Te–O–Te and Se–O–Se linkages and formation of TeO_3^- and SeO_3^- terminal groups.

2. Experimental

$70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$ (where R = potassium, sodium and lithium) glasses were prepared by melt-quenching technique. The materials were well mixed in appropriate proportions to form 5-g batches. The mixed proportions were ground in a mortar for homogeneity. Each batch was melted at temperatures in the range $715\text{--}800^\circ\text{C}$ for 30 min in a porcelain crucible in an electrically heated furnace. The melt was then quenched rapidly between thick stainless steel plates which are pre-heated at 200°C to form transparent glass plates. The amorphous nature of these glass samples was observed by X-ray diffraction (XRD, Bruker D8 Advance). Glasses were ground to obtain IR

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spectra (IR, Bruker Vector 22) in the range from 4000 to 500 cm^{-1} . The high-temperature Raman spectrometer (Raman, Horiba Jobin Youn; Model—Labram 633-nm laser wavelength) is used to characterize its structural behavior.

3. XRD patterns

Figure 1 shows the XRD pattern obtained from quenched glass of $70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$, where R = potassium composition is labeled as TSK2, R = sodium composition is labeled as TSN2 and R = lithium composition is labeled as TSL2. The XRD pattern shows no characteristic peak; therefore, all the glasses are amorphous in nature.

4. Results and discussion

4.1 Raman spectra

Raman spectra of all glasses containing potassium, sodium and lithium are recorded and shown in Figure 2. Their peak frequencies are presented in Table 1. In the present investigation, the main absorption bands are observed in the wave number range $470\text{--}481$, $663\text{--}675$ and $770\text{--}781\text{ cm}^{-1}$ for TSK2, TSN2 and TSL2 glasses, respectively. In general, in tellurium oxide-based glasses, the band around 460 cm^{-1} can be attributed to Te–O–Te or O–Te–O linkages. In accordance with our earlier studies on alkali boro tellurite glass system,²⁵ tellurium dioxide in 60 mol% shows a peak at 466 cm^{-1} that is attributed to the stretching vibration of B–O–B and Te–O–Te or O–Te–O linkages formed by sharing vertices of tellurium tetraoxide trigonal bipyramid (tbp) units or TeO_{3+1} polyhedra or tellurium trioxide trigonal pyramid (tp). Our earlier studies on $\text{TeO}_2\text{-GeO}_2\text{-WO}_3$ glassy system²⁶ showed that Raman lines at around $460\text{--}480\text{ cm}^{-1}$ are assigned to the stretching vibrations of Ge–O–Ge and Te–O–Te linkages in the form of tellurium tetraoxide (tbp) or TeO_{3+1} or tellurium

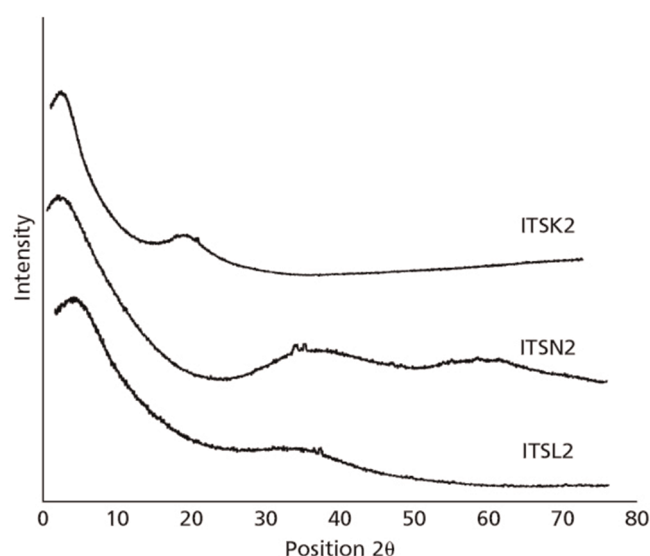


Figure 1. X-ray diffraction (XRD) spectrum of $70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$ (where R = potassium (K), sodium (Na) and lithium (Li)) glass system

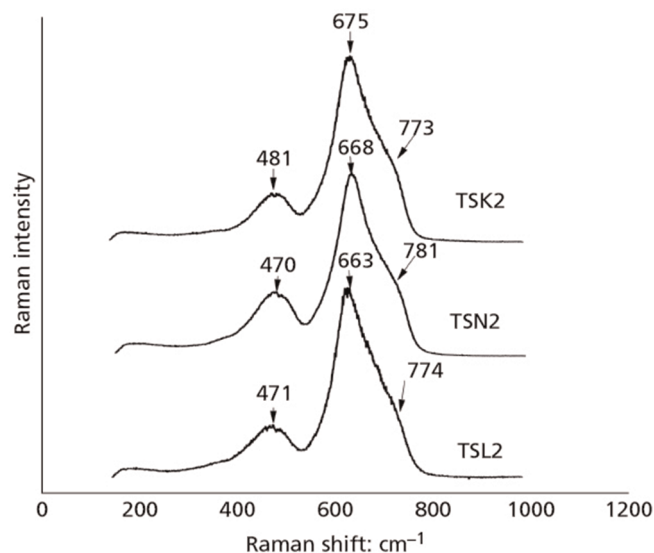


Figure 2. Raman spectra of $70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$ (where R = potassium (K), sodium (Na) and lithium (Li)) glass system

trioxide (tp). From the above results and studies in the literature, the peak around $481\text{--}470\text{ cm}^{-1}$, in the present study, can be strongly attributed to the stretching vibration of Te–O–Te linkages in the form of tbp, tellurium tetraoxide (tbp), TeO_{3+1} polyhedra or tellurium trioxide tp units. The peak at 670 cm^{-1} ²⁷ is assigned to the stretching mode of the TeO_3 tp units containing terminal Te–O bonds such as Te=O and Te=O– with non-bridging oxygen (NBO) atoms, the stretching mode of tellurium tetraoxide, tbp units with bridging oxygen atoms and bending mode of Te–O–Te or O–Te–O linkages.^{28,29} In the present study, the authors strongly attribute the bands at $663\text{--}675\text{ cm}^{-1}$ to the stretching mode of the TeO_3 tp units and stretching mode of tellurium tetraoxide tbp units with bridging oxygen atoms and bending mode of Te–O–Te or O–Te–O linkages. It has been reported that glasses containing tellurium showed Raman absorption lines from 755 to 775 cm^{-1} that attributed to the vibration modes of continuous network composed of tellurium tetraoxide (tbp) and stretching modes of tellurium and NBO atoms, TeO_{3+1} polyhedra or tellurium trioxide tp units. It was reported by Sekiya *et al.*³⁰ that glasses containing sodium and potassium selenite show Raman lines around 773 cm^{-1} due to the presence of selenite triangles but, unlike O=SeO_2 groups, they are isolated pyramidal groups with three equivalent Se–O bonds (SeO_3^{2-} groups). In the present

Glass code	Peak position: cm^{-1}		
TSK2	481	675	773
TSN2	470	668	781
TSL2	471	663	774

Table 1. Peak frequencies in Raman spectra of $70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$ (where R = potassium (K), sodium (Na) and lithium (Li)) glass system

study, the authors attribute the Raman lines around 773, 781 and 774 cm^{-1} due to the presence of selenium trioxide triangles but, unlike O=SeO_2 groups, they are isolated pyramidal groups with three equivalent Se-O bonds (SeO_3^{2-} groups).

4.2 IR spectra

IR spectra of all glasses are recorded and shown in Figure 3 (as absorbance units plotted against wave number). Their peak frequencies are presented in Table 2. There are mainly five broad absorption peaks that are observed in the present glass system. They are around 610 and 652 cm^{-1} for glass TSN2, 636 cm^{-1} for TSL2 and 780 cm^{-1} and 945 cm^{-1} for TSK2. In the case of tellurite glass network, the vibrational modes have two regions. The first characteristic band occurs in the wave number range $600\text{--}640\text{ cm}^{-1}$ for tellurium tetraoxide (tbp) units and the second band is found at $680\text{--}700\text{ cm}^{-1}$ for tellurium trioxide (tp) units.^{25,31} The absorption peak around $610\text{--}636\text{ cm}^{-1}$ is observed in the present study and is characteristic of Te-O stretching modes of tellurium tetraoxide (tbp) structural units. As reported by Bachvarova *et al.*,³⁵ the bands at 820 , 700 and 420 cm^{-1} are assigned to the vibrations of isolated selenium trioxide groups. The absorption band for the TSK2 glass

Glass code	Peak position: cm^{-1}		
TSK2	780	945	—
TSN2	610	652	—
TSL2	636	—	—

Table 2. Peak frequencies in infrared spectra of $70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$ (where R = potassium (K), sodium (Na) and lithium (Li)) glass system

is at 780 cm^{-1} and is attributed to the vibrations of isolated selenium trioxide groups.^{32,33} Probably, these selenite units take part in the amorphous network formation. Wave numbers corresponding to the weak bands are not shown in Figure 3. Peaks at $840\text{--}850\text{ cm}^{-1}$ for the glasses TSL2 and TSN2 could be related to the vibrations of isolated selenium trioxide groups.^{34,35} A strong band is observed for TSK2 glass at about 780 cm^{-1} with shoulder at $640\text{--}680\text{ cm}^{-1}$; the bands which are not shown in Figure 3 suggest that the deformed tellurium tetraoxide tetrahedra are the basic structural units in these glasses.³⁶⁻³⁸ Thus, there is a simultaneous existence of both tellurium tetraoxide and tellurium

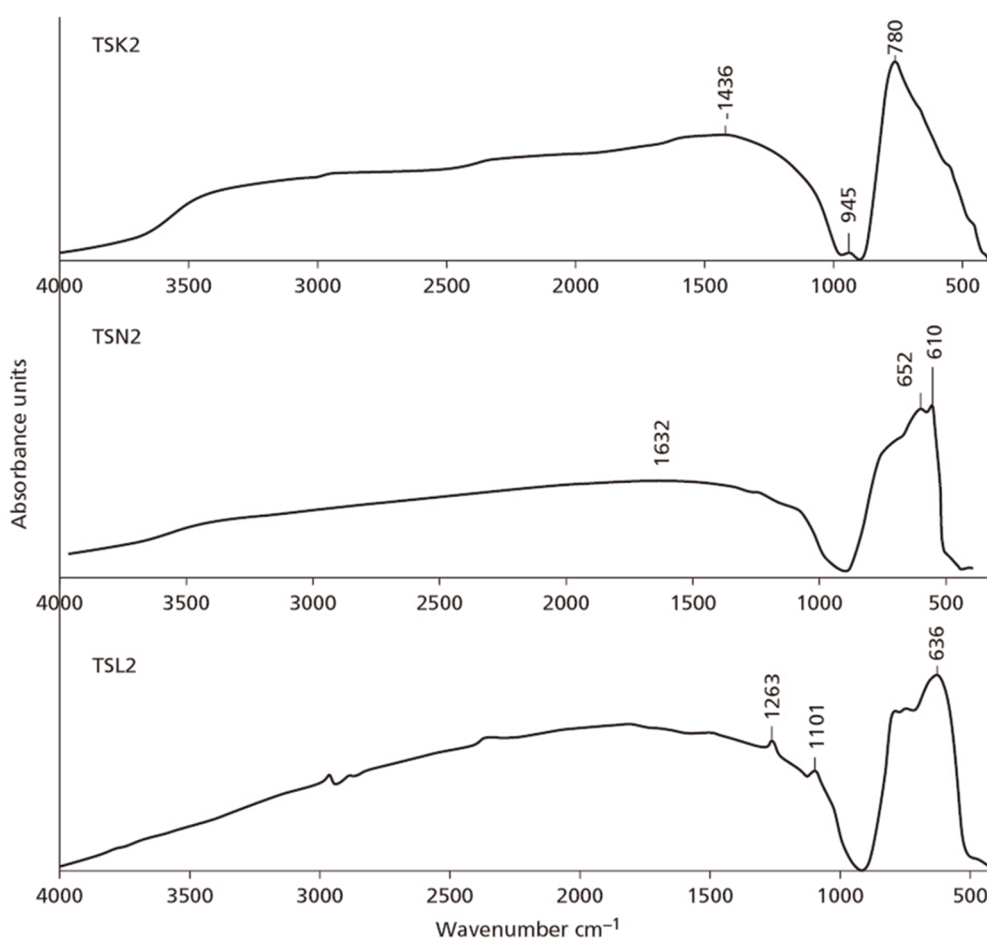


Figure 3. Infrared (IR) spectra of $70\text{TeO}_2\text{-}20\text{SeO}_2\text{-}10\text{R}_2\text{O}$ (where R = potassium (K), sodium (Na) and lithium (Li)) glass system

trioxide groups in the amorphous network in the glass considered in this study.³⁶ The bands around 500 and 470 cm⁻¹ could be related to the vibrations of different mixed bonds containing Te, Se and Mo.³⁶ According to Saddeek *et al.*,³⁸ the IR absorption in the range 470–490 cm⁻¹ is ascribed to the symmetrical stretching or bending vibrations of Te–O–Te linkages at corner-sharing sites. In the present study, the authors attribute the band at around 470–500 cm⁻¹ to the symmetrical stretching or bending vibrations of Te–O–Te linkages at corner-sharing sites. The weak bands at 950 and 890 cm⁻¹, which are observed only in the spectra of glass 2 are due to the vibrations of Mo₂O₈ (MoO₅) units.³⁶ In the present study, the authors observed weak band at 945 cm⁻¹ for the glass TSK2 due to vibrations of potassium oxide (K₂O) units.

5. Conclusions

The glass formation range was determined in 70TeO₂–20SeO₂–10R₂O where R = potassium, sodium and lithium in the glass system which are 10 mol% in alkali cation content. The introduction of alkali oxide in tellurium dioxide leads to a gradual reduction in the tellurium coordination from TeO₄ → TeO₃₊₁ → TeO₃ and a substantial change in glass structure in accordance with another glass former, the selenium dioxide. The addition of potassium, sodium and lithium to the tellurite selenite glass results in the cleavage of Te–O–Te and Se–O–Se linkages by the formation of TeO₃⁻ and SeO₃⁻ terminal groups, thereby leading to distortions in the glassy network, reducing its rigidity in the present glass system.

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