

THE STRUCTURAL STUDIES OF Er^{3+} : TeO_2 - Li_2O - PbO - Nd_2O_3 GLASS SYSTEM

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ABSTRACT

Series of Er^{3+} doped tellurite glass of the TeO_2 - PbO - Li_2O - Nd_2O_3 - Er_2O_3 system was successfully been made. The glass structure has been studied by means of FTIR and Raman spectroscopy. Seven significant vibrational peaks around 467,664,746,1456,1643,2368 and 3445 nm which correspond to the structural bonding of the glass are observed in a range of 400-4000nm. The peaks observed are consistent with the stretching and bending vibrations of the Pb-O, TeO_4 trigonal bipyramids, TeO_3 trigonal pyramids, Te-O-Pb and M-OH linkages respectively. Weak band at 1630 cm^{-1} is believed to be due to the M-OH group probably due to the OH trapped in the glass structure. The refractive indices are found to be around 1.91 and is strongly correlated to the glass structure.

INTRODUCTION

A unique properties of tellurite based glass due to their scientific and technical interest has attracted considerable attention amongst the researchers. Glass containing tellurium has been reported to be the most stable host for rare earth ions as compare to other glass system [1-3]. TeO_2 glasses are not only interesting from its practical application but also exhibit interesting behaviour in their glass structure and glass forming ability [4]. The doped Er^{3+} tellurite glasses are the subject of intense current research because of their interesting physical, thermal and optical properties. Structural studies in tellurite glasses are of great importance owing to the interrelation between the atomic arrangement and properties. Basically, there are two types of basic TeO_2 structure unit namely, TeO_4 trigonal bipyramids (tpb) and TeO_3 trigonal pyramid (tp) respectively.[5] This is shown Figure 1.

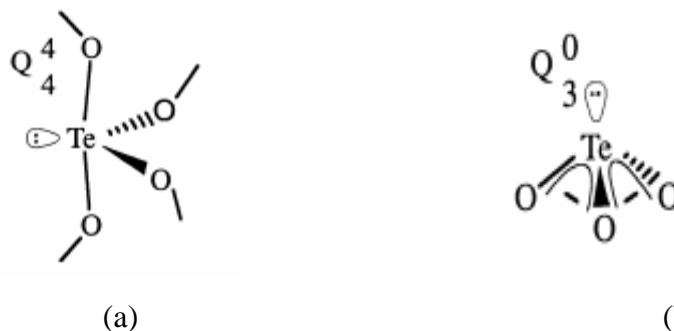


Figure 1: Basic tellurite structural unit (a) TeO_4 tpb, and (b) TeO_3 tp.

A variety of techniques in order to identify the glass structure has been reported elsewhere [6]. In this case, FTIR and Raman spectroscopy has been used effectively in probing the changes in basic glass structure. From the absorption spectra, the significant and valuable information on the atoms arrangement, the nature of chemical bonding and the changes in atomic configurations of the glass could be predicted [7] as well as the stretching and bending vibration mode of the glass host [5]. Meanwhile, the refractive indices obtained by using Sellmeier fitting were found having a strong correlation with glass structure. The aim of the present work is to study the structure of the TeO₂ glass consists of rare-earth element, Nd which strongly correlated to their optical properties.

EXPERIMENTAL DETAILS

Sample of tellurite glass co-doped with Nd³⁺/Er³⁺ ranging from 0% to 2.0 mol% were prepared from certified reagent grades of TeO₂ (99.95% purity), Li₂CO₃ (97%), PbO (98% purity) and Nd₂O₃ (99.995% purity) and Er₂O₃ (99.995% purity). The chemicals are firstly mixed thoroughly in Platinum crucible before being heated to about 1000 °C for half an hour. After the batch is completely melted, the melt is cast onto the preheated stainless steel plate to quench to form a glass. The glass is then immediately transferred to an annealing furnace at 300 °C where it is kept for five hours in order to relieve any residual stress to avoid embrittlement. The glass is then to be cool down to room temperature. Table 1 shows the nominal composition of the glass. The glass sample is then being cut and polished for the optical measurement. A Perkin Elmer 1600 Fourier Transform infra-red (FTIR) has been used to investigate the glass samples by using the KBr pellet techniques in the range of 400 – 4000 cm⁻¹. For the Raman spectroscopy, a Nd-YAG laser at their respective excitation wave length 810nm and 300mW has been used. The spectra are in frequency region of 100 – 1500 cm⁻¹. The Perkin Elmer UV Spectroscopy in the range of 400 – 900 nm has been used for the optical measurement.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The IR spectra for glass samples in the frequency range from 400-4000 cm⁻¹ are shown in Figure 2 and the absorption peaks position has been inserted in Table 1. From Fig.2, all glasses show great similarity in their general absorption shape with their respective peaks. It can be seen from the results that the IR bands shifted slightly to the higher frequencies immediately after the Er₂O₃ is introduced (S2-S5). From Figure 1, there are seven significant absorption peaks are observed. The absorption band in the 460-470 cm⁻¹ region has slightly shifted to higher frequency as the 0.5 mol% of Er³⁺ is added. The frequency of 460-470 cm⁻¹ region could be corresponds to the Pb-O bending vibration and remain unchanged as the Er₂O₃ contents increases from 0.5 mol% to 2.0 mol%. This is in agreement with the work by Alexander et al [8] in the binary PbO-Ga₂O₃ glass. A broad absorption bands around 660 cm⁻¹ to 670 cm⁻¹ region and 745 to 755 cm⁻¹ region, can be ascribed to the stretching vibrations of equatorial and axial Te-O bonds in the TeO₄ t_{bp} (disphenoid) and TeO₃ t_p respectively. Charton et. al.[9] in

their work also found a similar band around 620 cm^{-1} and a shoulder at about 770 cm^{-1} . These broad peaks are presumably due to the distribution of bond-angles, bond radius, fluctuation of the local electronic and atomic environment in the amorphous state [10]. As has been reported earlier [11], an addition of a modifier to TeO_2 glass may affect the concentration of Te-O bonds according to the type of added ions. This is true since in this glass, an addition of 0.5 mol% Er_2O_3 into the glass system shifted the sharp absorption peaks from 667 cm^{-1} to 664 cm^{-1} which might be due to the co-existence of the symmetric glass structure and the deformation of the TeO_4 group, whereas the shoulder around 752 cm^{-1} is found shifted to 746 cm^{-1} which could be assigned to the formation of TeO_3 group. This occurrence is caused by the perturbation of TeO_4 tbp unit into the TeO_3 through the formation of intermediate coordination of TeO_{3+1} [12].

Meanwhile, the absorption peak in the 1430 to 1460cm^{-1} region could be attributed to the Te-O-Pb stretching vibrations. An addition of oxide modifier and/or alkali modifier such as PbO and Li_2O into the Te glass network causes a change in Te coordination polyhedron from TeO_4 tbp to TeO_3 tp thus creating more non-bridging oxygen [13]. As reported by Miyaji and Sakka [14] who work on the Ga_2O_3 glass based on IR and Raman measurement, they found that most of Pb^{2+} ions may be incorporated in the system as the lead oxide break up the glass network. Meanwhile, an addition of Li_2O into the Te glass network seem do not affected the glass structure since no absorption peak has been shown. The vibration band are presumably shifted to the longer wavelength which eventually overlapped with the band around 3000 cm^{-1} [15] which does not exist in the Te glass spectra. The IR bands in the 1630 to 1650 cm^{-1} region and 3440 to 3460 cm^{-1} region are corresponded to the hydroxyl-metal bond as well as the hydroxyl-hydrogen bond stretching vibration respectively. Ryskin [16] in his work identified a band at 1650 cm^{-1} is assigned to the bending mode of water molecule in crystalline hydrated silicates. Kobayashi and his co-researcher [17] identified the existence of OH^{-1} absorption bands due to fundamental vibration for the absorption bands around 3400 cm^{-1} . Works done by O'Donnell [18] also found the bands around 3600 cm^{-1} which is due to the small amount of atmospheric water entrapped in the glass absorbed from the furnace atmosphere or contaminated batch materials. A weak absorption peak around 2373 cm^{-1} is a result of an absorption of the CO_2 on the surface of the sample [19].

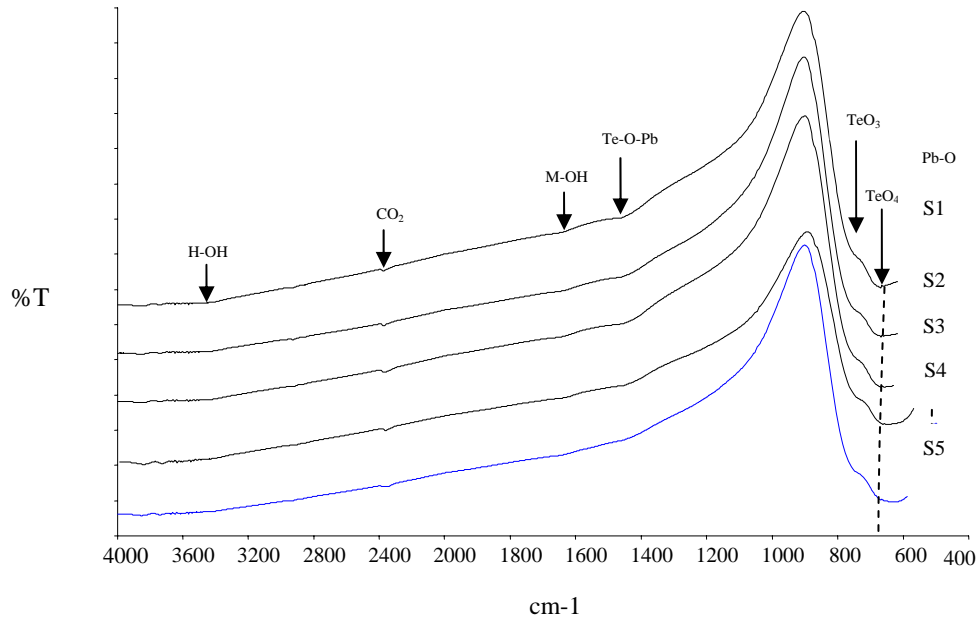


Figure 2: Infrared transmission spectra of $(78-x)\text{TeO}_2-10\text{PbO}-10\text{Li}_2\text{O}-2\text{Nd}_2\text{O}_3-x\text{Er}_2\text{O}_3$ glasses at various compositions.

Table 1: The FTIR peaks positions of the $(88-x)\text{TeO}_2-10\text{PbO}-2\text{Li}_2\text{O}-x\text{Nd}_2\text{O}_3$ glasses system

Sample	mol%					IR band (cm^{-1})						
	TeO_2	PbO	Li_2O	Nd_2O_3	Er_2O_3							
S41	78.0	10.0	10.0	2.0	-	469	667	752	1431	1638	2346	3456
S42	77.5	10.0	10.0	2.0	0.5	467	664	746	1454	1643	2368	3445
S43	77.0	10.0	10.0	2.0	1.0	467	664	746	1454	1643	2368	3445
S44	76.5	10.0	10.0	2.0	1.5	467	664	746	1454	1643	2368	3445
S45	76.0	10.0	10.0	2.0	2.0	467	664	746	1454	1643	2368	3445

Raman Spectroscopy

The study on the TeO_2 -based glass structure by Raman spectroscopy has been reported by many researchers [5,12,20]. The Raman spectra of tellurite glass are shown in Figure 3 and the corresponding peaks are summarized in Table 2. As shown in Fig. 3, it is clearly seen that there are three pronounced peaks that might be of interest occur around 190 to 210 cm^{-1} region, 640 to 660 cm^{-1} region and 740 to 750 cm^{-1} region in all glass samples. The presence of Raman bands in the 190 to 210 cm^{-1} can be assigned to both TeO_3 tp and Er-O [21]. The peak intensity at this region was observed to decrease with respect to mol% of Er^{3+} . A similar trend of results also been found by Sahar *et.al* [22] in their work. A decreasing of peak intensity may be attributed to the conversion

from TeO_4 tbp units to the other basic structural unit [23]. Meanwhile, the band around 640 to 660 cm^{-1} region is attributed to the stretching vibration of TeO_4 tbp unit and the band around 740 to 750 cm^{-1} region is corresponding to the perturbation of TeO_4 tbp unit into the TeO_3 tp unit respectively. As has been said earlier, an addition of Er^{3+} from 0.5mol% to 2.0mol% into the glass network tends to modify the structure by creating TeO_3 tp unit from TeO_4 tbp through the intermediate coordination TeO_{3+1} . This result is consistent with the previous FTIR absorption spectra which stated at similar respective peak the stretching vibration equatorial and axial tellurite-oxygen bonds in the TeO_3 tp and TeO_4 tbp have been occurred [11].

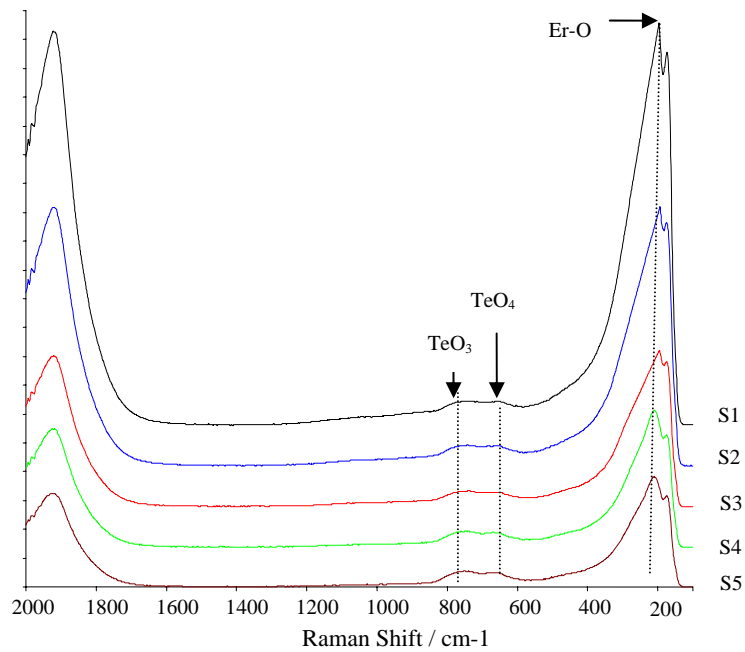


Figure 3: Raman Spectra of $(78-x)\text{TeO}_2-10\text{PbO}-10\text{Li}_2\text{O}-2\text{Nd}_2\text{O}_3-x\text{Er}_2\text{O}_3$ glasses at various composition.

Table 2: The Raman peaks of the $(78-x)\text{TeO}_2-10\text{PbO}-10\text{Li}_2\text{O}-2\text{Nd}_2\text{O}_3-x\text{Er}_2\text{O}_3$ glass system.

Sample	mol%					Raman Shift (cm^{-1})		
	TeO_2	PbO	Li_2O	Nd_2O_3	Er_2O_3			
S41	78.0	10.0	10.0	2.0	-	190	644	748
S42	77.5	10.0	10.0	2.0	0.5	194	648	754
S43	77.0	10.0	10.0	2.0	1.0	196	654	752
S44	76.5	10.0	10.0	2.0	1.5	210	668	752
S45	76.0	10.0	10.0	2.0	2.0	210	660	750

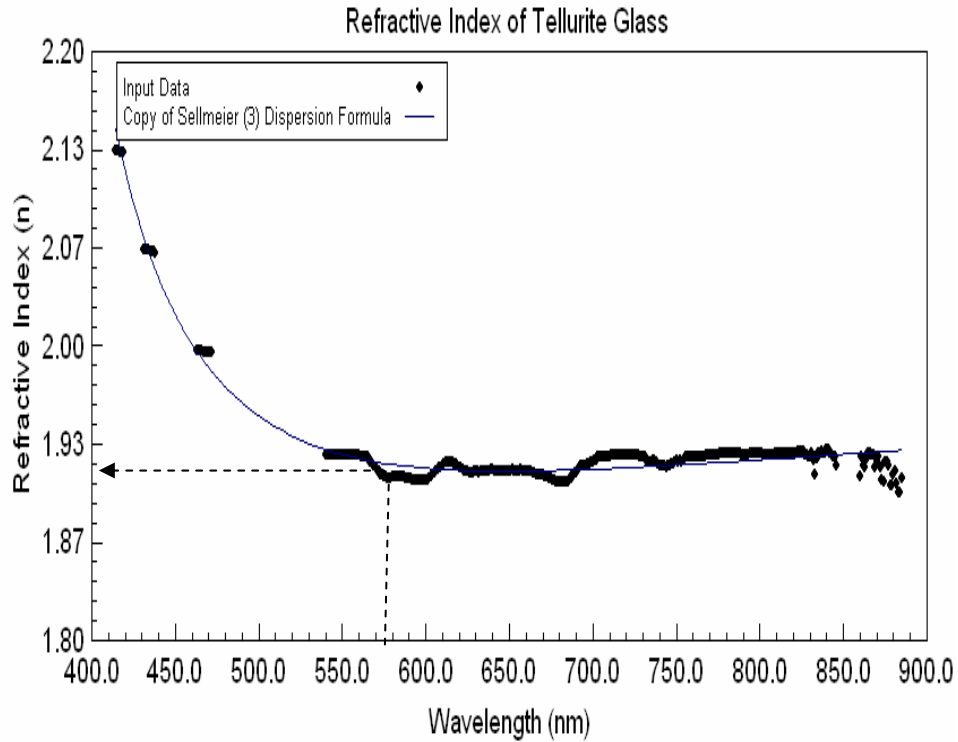


Figure 4: A typical graph of refractive index, n , against wavelength obtained through a Sellmeier fitting method.

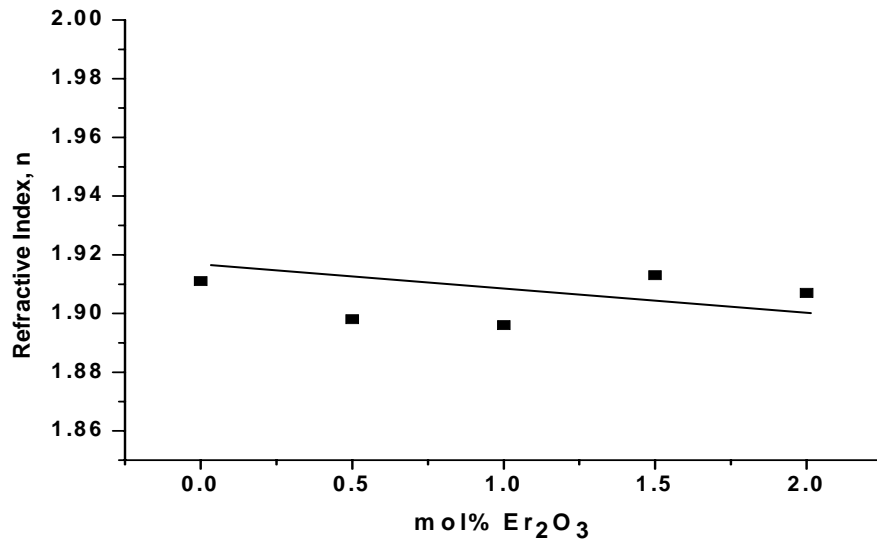


Figure 5: A decreasing trend of refractive index, n , measured at 570nm of wavelength with respect to mol% of Er_2O_3

UV Spectroscopy

The refractive index n which is related to the wavelength, λ , can be calculated using Sellmeier equation [24]:

$$n^2 = A + \frac{B\lambda^2}{\lambda^2 - C^2} + \frac{D\lambda^2}{\lambda^2 - E^2} \dots\dots\dots(1)$$

where A, B, C, D and E are the optical constants. C and E represent the effective resonance absorption wavelengths in the ultraviolet and infrared regions respectively. Using the spectra obtained from UV spectroscopy and then fitted into the Sellmeier equation (Eq.1), the refractive index can be obtained. A typical result of refractive index obtained by using Sellmeier fitting method is shown in Figure 4. As depicted in Fig.5, the refractive indices of tellurite glasses show a linear variation with respect to mol% of Er^{3+} . A strong correlation between refractive indices and the structural studies of the glass has been discussed elsewhere[25]. El-Mallawany *et. al* [26] in their work confirmed that refractive index has strong correlation to the glass structure. As the rare earth enter the glass network, it leads a formation of TeO_4 asymmetric polyhedron with one short and three elongated Te-O bonds and the TeO_3 trigonal pyramids having NBOs. Non-bridging oxygen is found to be more polarizable than bridging oxygen which has direct proportional between polarization and to the refractive index. Thus, the incorporation of rare earth into the tellurite glass system can actually changes the glass networks by creating more non-bridging oxygen (NBO) thus leads a formation of TeO_3 from TeO_4 . Therefore, an addition of rare earth ions such as Er^{3+} to the networks leads to the formation of dense packing of rare earth modifier into the host materials which have a direct effect on the increasing the refractive index [27]. Research done by Yanfei *et.al* (2008) also found the similar trend of results as the density and refractive indices increase with the increasing of WO_3 into the tellurite glass system [28]. Tokayuki *et.al* (1997) in their work ascribed that the refractive index is due to electronic transition of oscillators (bridging and non-bridging oxygen ions and cations in the ultraviolet region) and the lattice vibrations of the glass networks in the infrared region [29].

CONCLUSION

In the present work, tellurite glass of a system $(78-x)\text{TeO}_2\text{-PbO-Li}_2\text{O-Nd}_2\text{O}_3\text{-xEr}_2\text{O}_3$ has successfully been synthesized by melt-quenching techniques. From IR and Raman spectroscopy measurement, it is found that an addition of Er^{3+} from 0.5 mol% to 2.0 mol% into the glass system will change the glass structure by a deformation of TeO_4 tbp to TeO_3 bp and the formation of TeO_{eq} and TeO_{ax} . Meanwhile, the refractive indices decreases by the incorporation of Er^{3+} into the glass thus confirmed the occurrence of structural changes in the network unit.

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