

# Manifestation of Nd ions on the structure, Raman and IR spectra of (TeO<sub>2</sub>-MoO-Nd<sub>2</sub>O<sub>3</sub>) glasses

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The structure of [80TeO<sub>2</sub> + (20-x)MoO + xNd<sub>2</sub>O<sub>3</sub>] glasses, with  $x = 0, 4, 6, 10$  and  $12$  mol%, is studied in this work. Raman scattering in the spectral range ( $-2000$  to  $3500$  cm<sup>-1</sup>) and IR absorption spectra have been measured for crystalline TeO<sub>2</sub> and glasses, and their assignments were discussed and compared. Many vibrational modes were found active in both Raman and IR and their assignments for crystalline TeO<sub>2</sub> and for the glasses were discussed in relation to the tetragonal structure of crystalline  $\alpha$ -TeO<sub>2</sub>. Nd<sub>2</sub>O<sub>3</sub> was found to completely eliminate diffuse scattering and enhance the Raman scattering intensity. Anti-stokes Raman bands in the range  $-1460$  cm<sup>-1</sup> to  $-1975$  cm<sup>-1</sup> were observed for both (30Li<sub>2</sub>O + 70B<sub>2</sub>O<sub>3</sub> + xNd<sub>2</sub>O<sub>3</sub>) glasses and [80TeO<sub>2</sub> + (20 - x)MoO + xNd<sub>2</sub>O<sub>3</sub>] glasses and were attributed to some emission processes due to the doping of the glasses with Nd<sub>2</sub>O<sub>3</sub>.

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## 1. Introduction

Due to their stability, low crystallization rate, excellent transparency in a wide spectral region (3–18  $\mu$ m) and many other significant properties, Tellurite glasses are important in many technological applications. As reported in the literature, TeO<sub>2</sub> based glasses are considered as excellent materials for possible uses in non-linear optical devices, host materials for upconversion fluorescence of rare earth ions and high speed laser communication systems [1, 2]. Such importance of Tellurite glasses is in principle due to their specifically high electron-phonon anharmonicity [3]. The structure of binary (TeO<sub>2</sub>-MoO) glasses and (TeO<sub>2</sub>-MoO) crystalline systems and some other TeO<sub>2</sub>-based glasses have been studied by XRD analysis, IR, Raman scattering and DSC [4–10], where bond lengths, way of bonding and the interactions among TeO<sub>4</sub>, TeO<sub>3+1</sub>, TeO<sub>3</sub> and the glass modifier cations have been discussed.

TeO<sub>2</sub>-based glasses are known as good hosts for rare earth ions (e.g. Nd<sup>2+</sup>, Er<sup>3+</sup>) in possible uses for practical laser applications [11]. Upconversion fluorescence was observed for the first time in Tellurite glasses of the composition (70TeO<sub>2</sub>·30Na<sub>2</sub>O·1Er<sub>2</sub>O<sub>3</sub>), and Er<sup>3+</sup> ions were found to be relatively more important in Tellurite glasses than Nd<sup>2+</sup> [12, 13]. Some important properties of Er<sup>3+</sup> doped Tellurite glass fibers have been published and this work has attracted a strong attention because of its importance in increasing the transmission capacity of some high-speed communication systems [14, 15]. Upconversion fluorescence has been reported in

several Tellurite glasses doped with Ho<sup>3+</sup> and these glasses were expected to be used as upconversion laser materials [16].

Tellurite glasses containing GaO<sub>2</sub> are known as promising glasses of high thermal stability and chemical resistance and could be used in improving the fiber amplifier efficiency [17]. Glasses of the system (ZnF<sub>2</sub>-PbO-TeO<sub>2</sub>) show a high transparency in the 3 to 18  $\mu$ m region and they are considered as best materials for uses as optical components, filters, and laser windows [18]. Optical absorption and photoluminescence properties of Eu<sup>3+</sup>-doped (TeO<sub>2</sub>-ZnF<sub>2</sub>-PbO) glasses have been studied and different possible laser emission transitions were discussed [18–21].

Glasses of the composition [80TeO<sub>2</sub>-10Nb<sub>2</sub>O<sub>5</sub>-5Li<sub>2</sub>O-5K<sub>2</sub>O] doped with 0.5–10 mol% of Nd<sub>2</sub>O<sub>3</sub> have been studied by Raman scattering, DSC and were found to be more thermally stable as Nd<sub>2</sub>O<sub>3</sub> increases and this was attributed to an increase in the rigidity of the glasses with the addition of Nd<sub>2</sub>O<sub>3</sub> [22]. These glasses were suggested to be utilized as rare earth containing amplifying devices, where its emission cross-sections were reported to be the largest among oxide glasses. In the present work we study the effect of Nd<sub>2</sub>O<sub>3</sub> on the structure of [80TeO<sub>2</sub> + (20 - x)MoO + xNd<sub>2</sub>O<sub>3</sub>] glasses, with  $x = 0, 4, 6, 10$  and  $12$  mol% using FIR to MIR absorption in the range (80 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>) and Raman scattering in the spectral range ( $-2000$  cm<sup>-1</sup> to 3500 cm<sup>-1</sup>). The negative sign before the frequency values placed here and for the

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Raman spectra hereinafter means negative frequency shift.

## 2. Experimental

Glass samples of the composition  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$ , with  $x = 0, 4, 6, 10$  and  $12$  mol% have been prepared by fusing the respective proportions of the reagent grade oxides ( $\text{TeO}_2$ ,  $\text{MoO}$  and  $\text{Nd}_2\text{O}_3$  Aldrich chemicals 99.995%) in a platinum crucible in a preheated furnace at  $800^\circ\text{C}$  for about 30 min. After complete fusion, the melt was poured on a stainless steel plate at room temperature and quickly pressed by a similar plate. Bulk samples of  $\sim 2$  cm diameter and  $\sim 0.5$  mm thickness were obtained. Samples have not been subjected to any annealing process and its glassy state was confirmed using X-ray diffraction XRD. Glass samples are labeled in the present work as TNd0G, TNd4G, TNd6G, TNd10G and TNd12G, respectively for  $x = 0, 4, 6, 10$  and  $12$  mol%. The glass formation range GFR of the present system was found to contain up to 12 mol% of  $\text{Nd}_2\text{O}_3$ , and no glasses was obtained beyond this limit.

The FT-Raman and IR spectra were measured at room temperature for the as casting samples using BRUKER FT-Raman spectrometer of type RFS 100/S, which is attached to BRUKER-IFS 66/S spectrometer. The RFS 100/S version provides flexible sample handling and optimum FT-Raman performance. This system is equipped with a broad-range Quartz beam splitter; BRUKER's patented frictionless interferometer with its ROCKSOLID alignment provides high sensitivity and stability. The diode-pumped, air-cooled Nd-YAG laser source with maximum laser power of 1500 mW is controlled completely through software. The standard RFS 100/S configuration provides a spectral range of  $70\text{--}3600$   $\text{cm}^{-1}$  (Stokes' shift), and  $-100$  to  $-2000$   $\text{cm}^{-1}$  (anti-Stokes shift). Raman spectra of (as casting) bulk glass samples of the present work have been measured with a resolution of  $2$   $\text{cm}^{-1}$  using  $1064$  nm laser line with a power of 100 mW over the whole spectral range. The high precision air bearing interferometer provides high resolution to better than  $0.1$   $\text{cm}^{-1}$ . However, it was found that a resolution of  $2$   $\text{cm}^{-1}$  is appropriate for glasses of the present work. IR spectra in the range  $400$   $\text{cm}^{-1}$  to  $4000$   $\text{cm}^{-1}$  have been collected for powder glass samples dispersed in spec-pure KBr pallets with a resolution of  $2$   $\text{cm}^{-1}$  and a laser power of 100 mW at room temperature. FIR spectrum of crystalline  $\text{TeO}_2$  in the range  $(80\text{--}400$   $\text{cm}^{-1})$  has been collected by dispersing its powder in low-density polyethylene.

## 3. Results and discussions

Fig. 1 shows the Raman spectrum of crystalline  $\text{TeO}_2$  in the spectral range  $(-2000$   $\text{cm}^{-1}$  to  $+3500$   $\text{cm}^{-1})$ . As seen in the figure four strong Stokes' Raman bands are observed at 122, 149, 392 and 646  $\text{cm}^{-1}$ . These bands are also observed as anti-Stokes' bands with much lower relative intensities respectively at  $-122$ ,  $-148$ ,  $-391$  and  $-646$   $\text{cm}^{-1}$ . Figs 2a and b shows a comparison of the Raman spectrum from  $0\text{--}1000$   $\text{cm}^{-1}$  and the

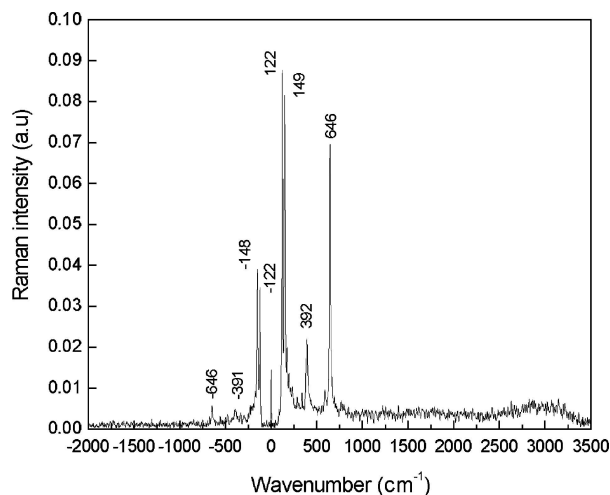


Figure 1 Raman spectrum of crystalline  $\text{TeO}_2$ .

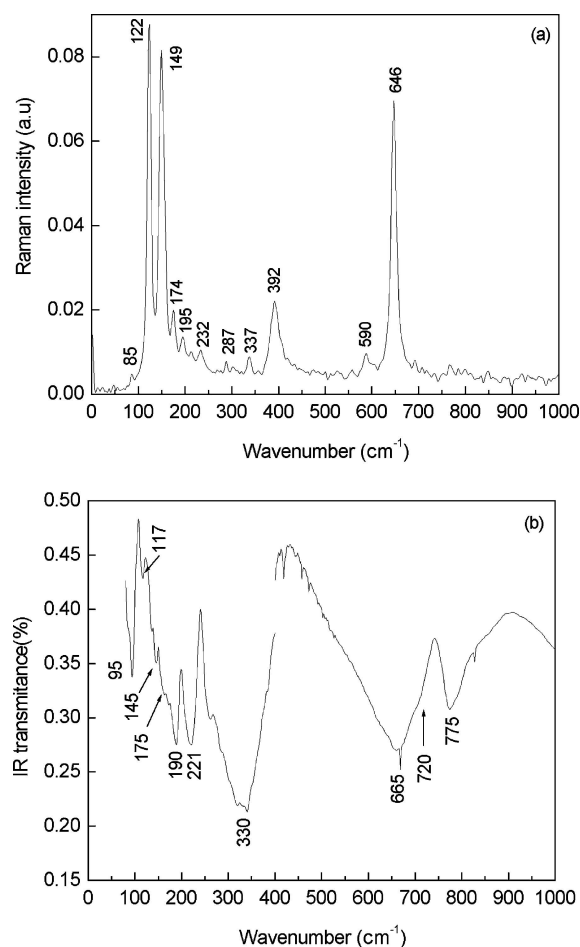


Figure 2 A blow up of the Raman spectrum of crystalline  $\text{TeO}_2$  (a), FIR-MIR spectra of crystalline  $\text{TeO}_2$  (b).

IR spectrum in the range  $80\text{--}1000$   $\text{cm}^{-1}$  of crystalline  $\text{TeO}_2$ . Crystalline  $\text{TeO}_2$  has two well known crystalline structures;  $\alpha\text{-TeO}_2$  of [ $D_{4h}^{14}$  (rutile),  $D_4^4$  and  $D_4^8$  (paratellurite)] space groups] and  $\beta\text{-TeO}_2$  (Tellurite) [6, 7, 10, 23, 24]. The two  $\alpha\text{-TeO}_2$  tetragonal structures with  $D_{4h}^{14}$  symmetry (rutile) or  $D_4^4$ ,  $D_4^8$  symmetry (paratellurite) have four vibrational modes active in both Raman and IR and assigned to the vibrational modes of the trigonal bipyramids tbps  $\text{TeO}_4$  tetrahedral units [2, 18–21]. In both structures, (rutile, paratellurite) the structural units are trigonal bipyramids tbps with two oxygen

atoms in the equatorial position and two oxygen atoms in the axial position. The tbps are deformed, where the Te atom is not at the center of the equatorial plane and the third position in this plane is occupied with a free electron pair.  $\delta$ -TeO<sub>2</sub> crystalline phase, and  $\gamma$ -TeO<sub>2</sub> orthorhombic metastable crystalline phase are known as well [23–26]. The relatively new  $\delta$ -TeO<sub>2</sub> and  $\gamma$ -TeO<sub>2</sub> crystalline phases have been investigated in studying the crystallization process of some TeO<sub>2</sub>-glasses [23].  $\gamma$ -TeO<sub>2</sub> crystalline phase was considered the most possible short range order structure for TeO<sub>2</sub> glasses due to its direct formation during heating of the glasses, the good correspondence of the Raman spectrum and the TeO<sub>2</sub>-glass with that of the  $\gamma$ -TeO<sub>2</sub> crystalline phase, and finally due to the best correspondence of the calculated vibrational state density distribution VSDD of the  $\gamma$ -TeO<sub>2</sub> phase and the TeO<sub>2</sub>-glass [23].

On the other hand, it has been well established that the TeO<sub>2</sub>-glass structure is composed of TeO<sub>4</sub> trigonal bipyramids (tbps) connected by vertices as the  $\alpha$ -TeO<sub>2</sub> crystalline phase and that the increase of the modifier content converts these TeO<sub>4</sub> tetrahedra to TeO<sub>3+1</sub> polyhedra and TeO<sub>3</sub> units [22, 27–29].

The Raman spectrum of crystalline TeO<sub>2</sub> measured in the present work, Fig. 1, is characteristic of  $\alpha$ -TeO<sub>2</sub> [22, 23] and could be assigned to the vibrational modes of the trigonal bipyramids tbps of the TeO<sub>4</sub> tetragonal units. The band at 392 cm<sup>-1</sup> is due to the axial bending vibrational mode (O<sub>ax</sub>-T-O<sub>ax</sub>)<sub>b</sub> and the band at 646 cm<sup>-1</sup> is due to the axial symmetric stretching vibrational mode (Te<sub>ax</sub>-O)<sub>s</sub> of the TeO<sub>4</sub> tetrahedra [18–21]. In Fig. 2b the IR band at 665 cm<sup>-1</sup> is corresponding to the Raman band at 646 cm<sup>-1</sup> attributed to the axial symmetric stretching vibrational mode (Te<sub>ax</sub>-O)<sub>s</sub>, Fig. 2a. The IR shoulder at ~720 cm<sup>-1</sup> and the resolved band at 775 cm<sup>-1</sup> observed in the MIR spectrum of crystalline TeO<sub>2</sub> are due to the equatorial symmetric stretching (Te<sub>eq</sub>-O)<sub>s</sub> and the equatorial antisymmetric stretching (Te<sub>eq</sub>-O)<sub>as</sub> vibrational modes [2, 18–21]. The strongest IR band of crystalline TeO<sub>2</sub> centered at 330 cm<sup>-1</sup> is observed relatively weak in the Raman spectrum at 337 cm<sup>-1</sup>, and the sharp IR peaks at 95, 190, and 221 cm<sup>-1</sup> are observed relatively weak in the Raman spectrum around the same positions as seen in Fig. 2. The dominant very strong Raman bands at 122, 149 cm<sup>-1</sup> are observed as unresolved shoulders in the IR spectrum at ~117 and ~145 cm<sup>-1</sup>. The activity of these vibrational modes of crystalline TeO<sub>2</sub> in both Raman and IR as seen here is characteristic of crystalline  $\alpha$ -TeO<sub>2</sub> [17, 18, 21, 23]. The small frequency differences between the bands observed in both Raman and IR spectra could be due to the fact that Raman scattering spectra were measured on as-casting bulk glass samples while the IR spectra have been collected from powder glass samples dispersed in KBr pellets.

Raman spectra of glasses are shown in Fig. 3. As seen in this figure, no Raman bands could be observed for the TNd0G glass sample (free of Nd<sub>2</sub>O<sub>3</sub>) due to the strong diffuse scattering around 3150 cm<sup>-1</sup>. Fig. 4a shows this diffuse scattering observed for this glass sample measured with different laser power values ranging from 100 mW to 550 mW. A laser power of 100 mW could

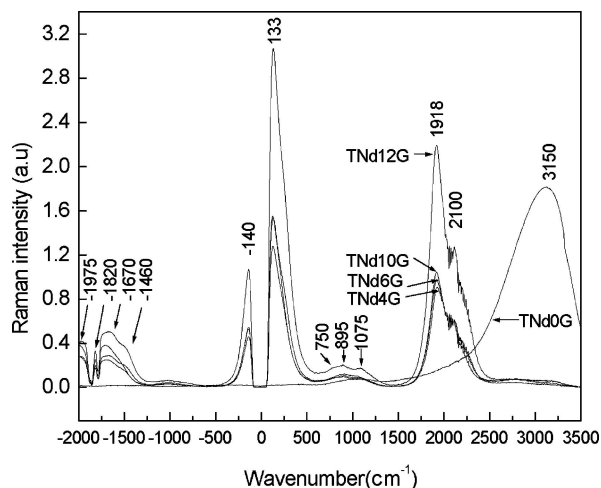


Figure 3 Raman spectra of the [80TeO<sub>2</sub> + (20 - x)MoO + xNd<sub>2</sub>O<sub>3</sub>] glasses, with x = 0, 4, 6, 10 and 12 mole%.

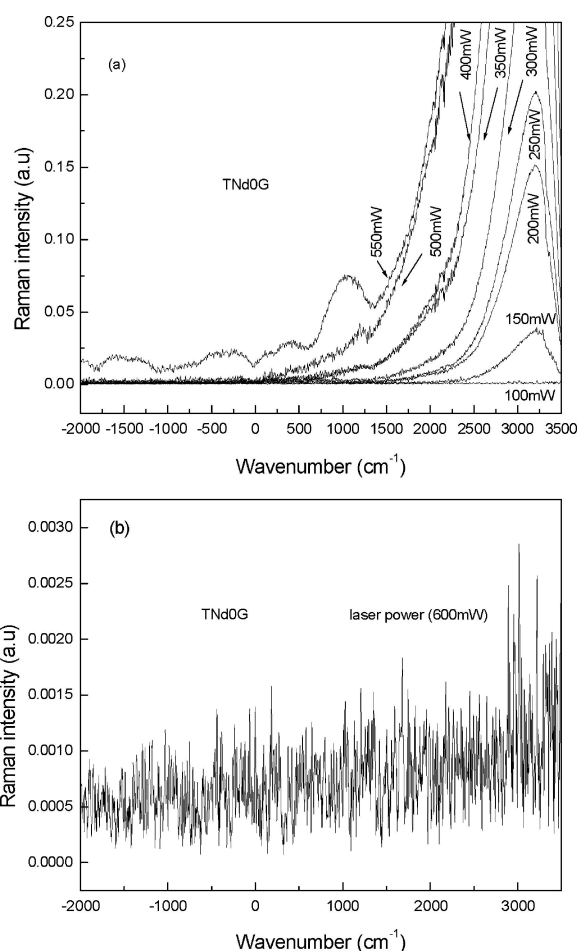


Figure 4 Raman spectra for the TNd0G glass, excited with different laser power values (a), with a laser power of 600 mW, (b).

not excite the Raman spectrum for this sample as shown in Fig. 4a. The very strong diffuse scattering around 3150 cm<sup>-1</sup> which increases with the laser power from 150 mW to 550 mW, Fig. 4a, made it hard to detect the Raman bands for this sample. Only with a laser power of 550 mW, a few Raman bands started to be observable between -2000 cm<sup>-1</sup> and +1500 cm<sup>-1</sup>. We tried to overcome diffuse scattering by increasing the laser power to 600 mW. However, diffuse scattering dominated the whole range and no spectrum could

be observed at all as seen in Fig. 4b. It seems that the thermal effect of the high power laser (600 mW) shining the sample may have ruptured the glass structure and resulted in no photon scattering. Raman spectra for other glass compositions (TNd4G, TNd6G, TNd10G, TNd12G), shown in Fig. 3, were easily collected with a laser power of 100 mW.

The Raman spectra of the glasses doped with  $\text{Nd}_2\text{O}_3$  (TNd4G, TNd6G, TNd10G, TNd12G) show very strong Raman bands at 2100, 1918, 133, -140, -1460, -1670, -1820 and -1975  $\text{cm}^{-1}$  as shown in Fig. 3. These bands are not observed for crystalline  $\text{TeO}_2$  as shown in Fig. 1. It is clear from Fig. 3 that the addition of  $\text{Nd}_2\text{O}_3$  enhanced the Raman intensities of all bands and completely eliminated the diffuse scattering shown by the TNd0G glass sample. The Raman intensities of all bands are increasing as  $\text{Nd}_2\text{O}_3$  content increases and show maximum values for the sample containing the highest content of  $\text{Nd}_2\text{O}_3$  as shown in Fig. 3. The broad band centered at 133  $\text{cm}^{-1}$  seen in Fig. 3 may represent an overlap of the Stokes' Raman bands of crystalline  $\text{TeO}_2$  at (122, 149  $\text{cm}^{-1}$ ) seen in Fig. 1. Similarly, the anti-Stokes band of the glass samples at -140  $\text{cm}^{-1}$  is an overlap of the two anti-Stokes bands of crystalline  $\text{TeO}_2$  at (-122, -148  $\text{cm}^{-1}$ ). These two bands represent the most intense vibrations of crystalline  $\text{TeO}_2$  and its strong appearance in all glass samples suggests that the short-range order SRO of these glasses is a disordered version of crystalline  $\alpha\text{-TeO}_2$ . The broadening and the asymmetry of the Raman bands of the glasses at +133  $\text{cm}^{-1}$  and -140  $\text{cm}^{-1}$  are due to its disordered nature, where acoustic Raman AR bands arising from the disordered nature could be embedded under these strong peaks. AR bands at frequencies of  $\sim 40$  to  $100 \text{ cm}^{-1}$  known as Boson peaks, associated to light scattering due to acoustic-like vibrations of the disordered structure, have been seen in many oxide glasses including Tellurites and its origin still a matter of debate [27, 30–34]. These AR peaks are usually seen overlapped with some Raman modes of vibrations of the glass matrix, that is, vibrational modes of the basic structural units of the glass former and the glass modifier cations. A low frequency band at  $\sim 130 \text{ cm}^{-1}$  has been observed in a previous work on ( $\text{GeO}_2\text{-TeO}_2\text{-PbO-CaO}$ ) glasses and was assigned to the modifier-nonbridging oxygens NBO vibrations of the (Pb–O) bonds [27].

On comparison of Figs 2a and 3, it is interesting to notice that the relatively weak features in the range 174–337  $\text{cm}^{-1}$  and the very strong bands at 392, 646  $\text{cm}^{-1}$  characteristics of  $\text{TeO}_4$  tbps of crystalline  $\alpha\text{-TeO}_2$ , Fig. 2a, have been disappeared in the spectra of the glasses. That is,  $\text{Nd}_2\text{O}_3$  is strongly affecting the short-range order SRO structure of the present glasses. In Fig. 3, the weak broad band centered around 750  $\text{cm}^{-1}$  observed for all glasses containing  $\text{Nd}_2\text{O}_3$  could be an envelope assigned to the  $(\text{Te}_{\text{eq}}\text{-O})_{\text{s}}$  and the  $(\text{Te}_{\text{eq}}\text{-O})_{\text{as}}$  vibrational modes of some amount of  $\text{TeO}_{3+1}$  polyhedra and/or  $\text{TeO}_3$  trigonal pyramids tps formed in the glasses of the present work [2, 18–21]. A Raman band in the range 420–450  $\text{cm}^{-1}$  have been observed in a previous work for

many  $\text{TeO}_2$ -glasses and was assigned to the symmetric stretching and bending vibrations of (Te–O–Te) linkages which are formed by vertex-sharing of  $(\text{TeO}_4)$ ,  $(\text{TeO}_{3+1})$  polyhedra and  $(\text{TeO}_3)$  units [27, 29]. However, this band does not appear in the spectra of the present work and could be embedded underneath the very intense dominant Raman peak at 133  $\text{cm}^{-1}$ . Such apparent discrepancies may be due to the fact that some modes could be caused by anharmonic combinations of frequencies, which are typical for Tellurite glasses [35].

Two other broad bands with low relative intensities are observed in the Raman spectra of the glasses in Fig. 3 at  $\sim 895$ ,  $\sim 1075 \text{ cm}^{-1}$ . These two bands could be assigned respectively to the stretching vibrations of (Mo=O) bonds of deformed  $\text{MoO}_6$  octahedra and to the vibrations of (Mo–O–Mo) bridging bonds [28]. The strong band at 1918  $\text{cm}^{-1}$  and the shoulder centered around 2100  $\text{cm}^{-1}$  observed for all glasses have no specific assignments and need to be more clarified and discussed.

Figs 5a and b shows the Raman intensity and the bandwidth at half maximum BWHM of the Raman bands as a function of  $\text{Nd}_2\text{O}_3$ . As shown, the Raman intensity of almost all bands shows maximum

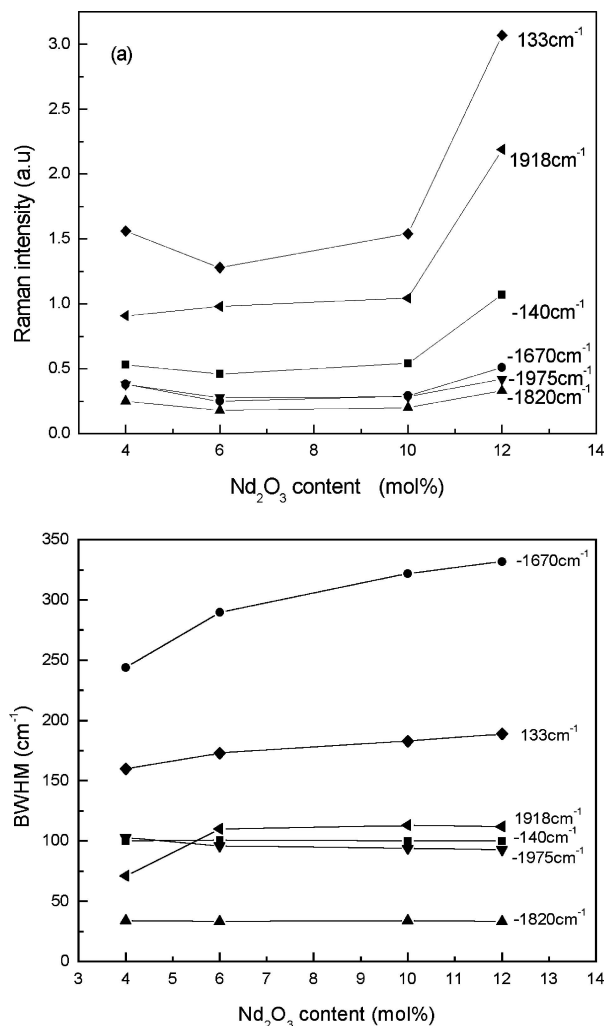


Figure 5 Raman intensity (a), BWHM (b) as a function of  $\text{Nd}_2\text{O}_3$  content for the  $[\text{80TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses.

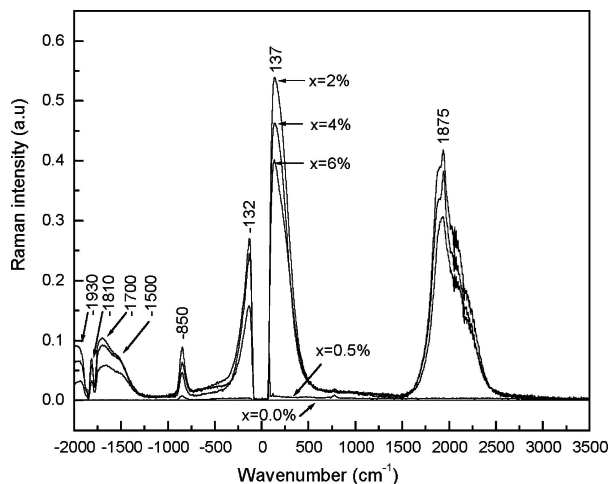


Figure 6 Raman spectra of  $(30\text{Li}_2\text{O} + 70\text{B}_2\text{O}_3 + x\text{Nd}_2\text{O}_3)$  glasses, with  $x = 0, 0.5, 2, 4$  and  $6$  mole%.

values for the sample with the highest content of  $\text{Nd}_2\text{O}_3$  (TNd12G). Also, the BWHM of the bands at  $-1670\text{ cm}^{-1}$ ,  $133\text{ cm}^{-1}$  and at  $1918\text{ cm}^{-1}$  are increasing as  $\text{Nd}_2\text{O}_3$  increases. This dependence of the Raman intensity and the BWHM on  $\text{Nd}_2\text{O}_3$  content shows the strong effect of  $\text{Nd}_2\text{O}_3$  on the structure of the glasses.

To show the effect of  $\text{Nd}_2\text{O}_3$  on the Raman scattering from a different oxide glass system, we present the Raman spectra of  $(30\text{Li}_2\text{O} + 70\text{B}_2\text{O}_3 + x\text{Nd}_2\text{O}_3)$  glasses, with  $0 \leq x \leq 6$  mole%, measured in a previous work and shown in Fig. 6 [36], to be compared with the Raman spectra of  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses of the present work. As shown in Fig. 6, for the glass sample free of  $\text{Nd}_2\text{O}_3$  ( $x = 0$ ) no Raman bands are observed at all, and for the glass sample with  $x = 0.5$  mole% some very weak bands are hardly seen. Glasses with  $x = 2, 4$  and  $6$  mole% of  $\text{Nd}_2\text{O}_3$  show strong Stokes' bands at  $137$  and  $1875\text{ cm}^{-1}$ . The relative intensities and frequency positions of these two bands are very close to the bands at  $133$  and  $1918\text{ cm}^{-1}$  of the  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses shown in Fig. 3. The anti-stokes bands observed at  $(-1500, -1700, -1810$  and  $-1930\text{ cm}^{-1})$  for  $(30\text{Li}_2\text{O} + 70\text{B}_2\text{O}_3 + x\text{Nd}_2\text{O}_3)$  glasses with  $x = 2$  to  $6$  mol% are very similar to those of the  $(\text{TeO}_2 + \text{MoO} + \text{Nd}_2\text{O}_3)$  glasses seen in Fig. 3. The closed correspondence of frequency positions and relative intensities of these Raman bands in two completely different glassy materials manifests the strong effect of  $\text{Nd}_2\text{O}_3$  on the structure of these glasses.

Figs 7a and b show a comparison of the anti-stokes Raman bands of the  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses and  $(30\text{Li}_2\text{O} + 70\text{B}_2\text{O}_3 + x\text{Nd}_2\text{O}_3)$  glasses. The relative intensities, positions and the closed similarity of the anti-stokes bands in these completely different glass matrices suggest that these bands are due to some emission processes due to  $\text{Nd}^{++}$  ions. Further Raman and optical absorption measurements on  $[(\text{Li}_2\text{O} - \text{B}_2\text{O}_3 - \text{Nd}_2\text{O}_3), (\text{TeO}_2 - \text{MoO} - \text{Nd}_2\text{O}_3)]$  glasses and its dependence on composition and temperature are being now under consideration to get quantitative information about any possible emission processes due to  $\text{Nd}_2\text{O}_3$ .

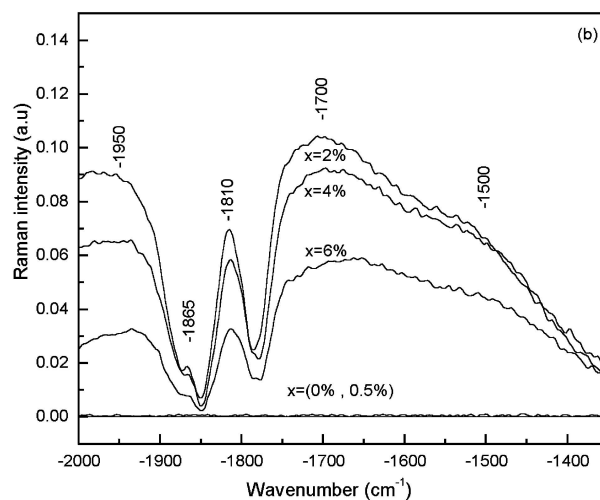
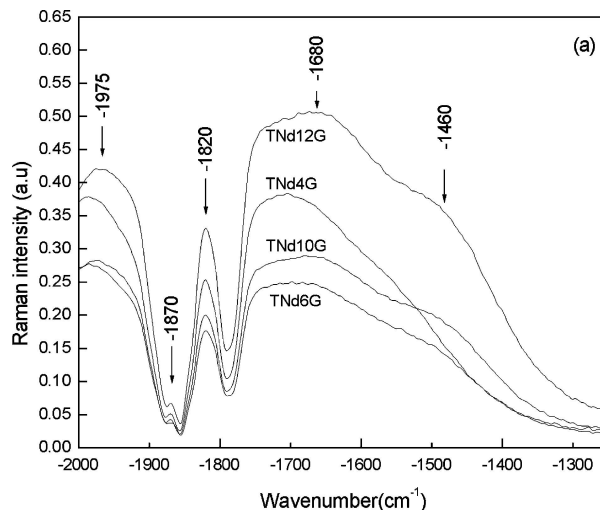


Figure 7 Enlarged anti-stokes Raman spectra of the  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses (a), and the  $(30\text{Li}_2\text{O} + 70\text{B}_2\text{O}_3 + x\text{Nd}_2\text{O}_3)$  glasses (b).

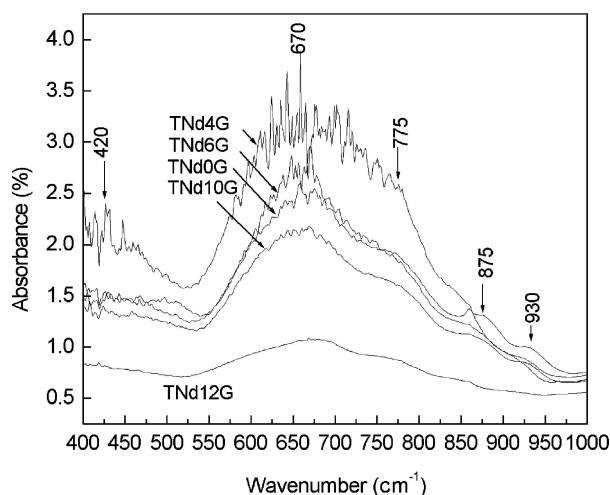


Figure 8 MIR spectra of the  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses, with  $x = 0, 4, 6, 10$  and  $12$  mole%.

Fig. 8 shows the IR absorption spectra of the glasses. The main band at  $\sim 670\text{ cm}^{-1}$  is due to the axial symmetric stretching vibrational modes  $(\text{Te}_{\text{ax}} - \text{O})_s$  of  $\text{TeO}_4$  tetrahedra [2, 18–21]. This band is corresponding to the IR band at  $665\text{ cm}^{-1}$  and to the Raman band at  $646\text{ cm}^{-1}$  of crystalline  $\text{TeO}_2$  observed in Figs 2a and b. The unresolved IR shoulder at  $\sim 750$

to  $\sim 775\text{ cm}^{-1}$  observed for all glasses could be an envelope corresponding to the equatorial symmetric vibrations ( $\text{Te}_{\text{eq}}\text{-O}$ )<sub>s</sub> and the equatorial asymmetric vibrations ( $\text{Te}_{\text{eq}}\text{-O}$ )<sub>as</sub> observed in the Raman spectra of the glasses shown in Fig. 3. The IR broad band centered at  $\sim 420\text{ cm}^{-1}$  for all glasses has been observed in some previous work on tellurite glasses and was assigned to the (glass former–glass modifier) bridging bonds [28, 30]. For the glasses of the present work, it could be assigned to the ( $\text{Te}\text{-O}\text{-Mo}$ ) and/or ( $\text{Te}\text{-O}\text{-Nd}$ ) stretching vibrations where the modifier cations (Mo and/or Nd) may incorporate in the glass matrix by bonding with  $\text{TeO}_4$  tetrahedra through Oxygens.

Two other bands with low relative intensities are observed in the IR spectra of the glasses in Fig. 8 as shoulders at  $\sim 875$  and  $\sim 930\text{ cm}^{-1}$ . These two bands could be assigned respectively to the stretching vibrations of ( $\text{Mo}=\text{O}$ ) bonds of the deformed  $\text{MoO}_6$  octahedra and to the vibrations of ( $\text{Mo}\text{-O}\text{-Mo}$ ) bridging bonds [28]. Crystalline  $\text{MoO}$  consists of deformed  $\text{MoO}_6$  octahedra and is known to have a strong IR band at  $985\text{ cm}^{-1}$  and two bands at  $\sim 870\text{ cm}^{-1}$  and  $813\text{ cm}^{-1}$  [29]. An IR band at  $\sim 910\text{ cm}^{-1}$  has been previously observed in a binary  $\text{TeO}_2\text{-MoO}$  glasses and was assigned to  $\text{Mo}\text{-O}$  non-bridging stretching modes [28].

#### 4. Conclusions

The Glass formation range of  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses, with  $x = 0, 4, 6, 10$  and  $12\text{ mol}\%$ , was found to contain an upper limit of  $12\text{ mol}\%$  of  $\text{Nd}_2\text{O}_3$ . The effect of  $\text{Nd}_2\text{O}_3$  on the structure of these glasses has been studied in this work using Raman scattering and IR spectroscopy. The axial symmetric stretching vibrations ( $\text{Te}_{\text{ax}}\text{-O}$ )<sub>s</sub>, the equatorial symmetric vibrations ( $\text{Te}_{\text{eq}}\text{-O}$ )<sub>s</sub> and the equatorial antisymmetric vibrations ( $\text{Te}_{\text{eq}}\text{-O}$ )<sub>as</sub> have been observed for crystalline  $\text{TeO}_2$  in both Raman and IR. Assignments of the Raman and the IR spectra of crystalline  $\text{TeO}_2$  have been compared and were found characteristics of  $\alpha\text{-TeO}_2$ . The presence, positions and intensities of many vibrational modes in both Raman and IR spectra of the glasses and the possible roles of  $\text{Nd}_2\text{O}_3$  and  $\text{MoO}$  have been discussed in relation to the tetragonal structure of crystalline  $\alpha\text{-TeO}_2$  with  $D_{4h}^{14}$  symmetry (rutile) or  $D_4^4$  symmetry (paratellurite). It was found that, the addition of  $\text{Nd}_2\text{O}_3$  very much enhances the Raman intensities and completely eliminates the diffuse scattering shown by the  $\text{Nd}_2\text{O}_3$  free sample. The relative intensities and the BWHM of the Raman Stokes' bands at  $133\text{ cm}^{-1}$ ,  $1918\text{ cm}^{-1}$  and of the anti-Stokes bands at  $-140\text{ cm}^{-1}$ ,  $-1670\text{ cm}^{-1}$ ,  $-1820\text{ cm}^{-1}$ ,  $-1975\text{ cm}^{-1}$  of the glasses were found dependent on  $\text{Nd}_2\text{O}_3$  content with maximum values for the sample with the highest content of  $\text{Nd}_2\text{O}_3$ . The anti-Stokes Raman bands of  $(30\text{Li}_2\text{O} + 70\text{B}_2\text{O}_3 + x\text{Nd}_2\text{O}_3)$  glasses and  $[80\text{TeO}_2 + (20 - x)\text{MoO} + x\text{Nd}_2\text{O}_3]$  glasses have been compared. It has been suggested that these bands are strongly related to  $\text{Nd}_2\text{O}_3$  and are attributed to some emission processes of  $\text{Nd}^{++}$  ions. Further Raman and optical absorption measurements and quantitative anal-

ysis will be considered in a future work on these glass systems.

#### References

1. H. NASU, O. MATSUSHITA, K. KAMIYA and H. KUBODERA, *J. Non. Cryst. Solids* **124** (1990) 275.
2. S. H. KIM, T. YOKA and S. SAKA, *J. Amer. Ceram. Soc.* **76** (1993) 865.
3. I. V. KITIK, J. KASPERCZYK and K. PLUCINSKI, *J. Opt. Soc. America B* **16** (1999) 1719.
4. H. HIROSHI, I. MICHIIHISA and T. YOSHIDA, *J. Non. Cryst. Solids* **86** (1986) 327.
5. E. F. LAMBSON, G. A. SANDERS, B. BRIDGE and R. A. ELMALLAWANY, *J. Non. Cryst. Solids* **69** (1984) 117.
6. S. NEOV, E. GREVASSIMOVA and B. SYDZHIMOV, *Phys. Status Solidi (a)* **76** (1983) 297.
7. Y. DIMITRIEV, V. DIMITROV and M. ARANUDOV, *J. Mat. Sci.* **18** (1983) 1353.
8. I. SHALTOUT, YI TANG, R. BRAUNSTEIN and A. M. ABU EL-AZM, *J. Phys. Chem. Solids* **56** (1995) 141.
9. I. SHALTOUT, YI TANG, R. BRAUNSTEIN and E. E. SHAISHA, *J. Phys. Chem. Solids* **57** (1996) 1223.
10. I. SHALTOUT, *J. Mat. Sci.* **35** (2000) 323.
11. M. J. WEBER, J. D. MYERS and D. H. BLACKBURN, *J. Appl. Phys.* **52** (1981) 2944.
12. S. TANABE, K. HIRAO and N. SOGA, *J. Non. Cryst. Solids* **122** (1990) 79.
13. H. NII, K. OZAKI, M. HERREN and M. MORITA, *J. Lumin.* **76/77** (1998) 116.
14. A. MORI, Y. OHISHI and S. SUDO, *Electron. Lett* **33** (1997) 863.
15. L. L. NEINDRE, SHIBIN JIANG, BOR-CHYUAN HWANG, TABLUO and JASON WATSON, *J. Non. Cryst. Solids* **255** (1999) 97.
16. K. HIRAO, S. KOSHIMOTO, K. TANAKA, S. TANABE and N. SOGA, *J. Non. Cryst. Solids* **139** (1992) 151.
17. J. RULLER and J. SHELBY, *J. Phys. Chem. Solids* **33** (1992) 177.
18. V. RAVI KUMAR and N. VEERAIHAH, *J. Phys. Chem. Solids* **59** (1998) 91.
19. V. RAVI KUMAR, N. VEERAIHAH, B. APPA RAO and S. BHUDDUDU, *J. Mat. Sci.* **33** (1998) 2659.
20. G. AMARNATH, S. BUDDHUDU and F. G. BRAYANT, *J. Lumin.* **15** (1991) 17.
21. G. AMARNATH, S. BUDDHUDU and F. G. BRAYANT, *J. Non. Cryst. Solids* **122** (1990) 86.
22. FABIA C. CASSANJES, YOUNES MESSADDEQ, LUIZ F. C. DE OLIVEIRA, LILIA C. COURROL, LAERCIO GOMES and SIDNEY J. L. RIBEIRO, *J. Non. Cryst. Solids* **1247** (1999) 58.
23. O. NOGUERA, T. MERLE-MEJEAN, A. P. MIRGORODSKY, M. B. SMIRNOV, P. THOMAS and J. C. CHAMPARNAUD-MESJARD, *J. Non. Cryst. Solids* **330** (2003) 50.
24. R. A. F. EL-MALLAWANY, "Tellurite Glasses Handbook: Properties and Data, CRC," Boca Raton, FL, 2002.
25. S. BLANCHANDIN, P. MARCHET, P. THOMAS, J. C. CHAMPARNAUD-MESJARD, B. FRIT and A. CHAGRAOUI, *J. Mat. Sci.* **34** (1999) 4285.
26. J. C. CHAMPARNAUD-MESJARD, S. BLANCHANDIN, P. THOMAS, A. MIRGORODSKY, T. MERLE-MEJEAN and B. FRIT, *J. Phys. Chem. Solids* **61** (2000) 1499.
27. C. DUVERGER, M. BOUZAOUI and S. TURELL, *J. Non. Cryst. Solids* **220** (1997) 169.
28. T. SEKIYA, N. MOCHIDA and A. SOEJIMA, *J. Non. Cryst. Solids* **191** (1995) 115.
29. T. SEKIYA, N. MOCHIDA, A. OHTSUKA and M. TONOKAUA, *J. Non. Cryst. Solids* **191** (1995) 128.
30. Y. DIMITRIEV, J. C. J. BART, V. DIMITROV and M. ARNAUDOV, *Z. Anorg. Allg. Chem.* **479** (1981) 229.
31. M. E. LINES, *J. Non. Cryst. Solids* **89** (1987) 143.

32. M. E. LINES, A. E. MILLER, K. NASSAU and K. B. LYONS, *J. Non. Cryst. Solids* **89** (1987) 163.
33. A. E. MILLER, K. NASSAU, K. B. LYONS and M. E. LINES, *J. Non. Cryst. Solids* **99** (1988) 289.
34. B. V. R. CHOWDARI and P. PRAMODA KUMARI, *J. Phys. Chem. Solids* **58**(3) (1997) 515.
35. I. V. KITZYK and B. SHARAOUI, *Phys. Rev* **B60** (1999) 942.
36. G. E. KHALIL, G. A. ABDEL FATTAH, M. SALAH SHAFIK and Y. BADR, "3rd workshop on photonics and its applications", IEEE, Cairo, 5 Jan.(2002), IEEE Catalog No:01EX 509.

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