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Physical and structural properties of glasses in the TeO_2–TiO_2–Nb_2O_5 system

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Abstract

Twelve glasses in the TeO_2–TiO_2–Nb_2O_5 system have been prepared. The glass forming region in the TeO_2–TiO_2–Nb_2O_5 ternary system was determined. The structural role of each component was studied by FTIR and some of their physical properties (density, molar volume, oxygen molar volume, transition temperature, thermal expansion coefficient, optical absorption and energy gap) were determined.

The glass structure is mainly built by [TeO_4] groups, while Nb^{5+} and Ti^{4+}-ions play as network modifiers. As the Nb_2O_5 and TiO_2 concentration increases, [TeO_4] groups progressively change to [TeO_3] groups as a consequence of the network opening. The contribution of the three ions to the oxygen molar volume follows the order: $Te^{4+} > Ti^{4+} > Nb^{5+}$. TiO_2 incorporation and even more Nb_2O_5 improve the glasses thermal stability and the network reinforcement. TiO_2 is the component which contributes in the highest extent to decrease the glass energy gap.

Keywords: Glass; Tellurites; Niobates; Spectroscopy; Thermal properties

1. Introduction

First systematic studies on tellurite glasses, initiated by Stanworth and co-workers,[1,2] were performed by Imaoka[3] and Vogel et al.[4] They determined the limits of the glass forming area for several binary and ternary systems and some of their optical properties as well. Recently, the interest on tellurite glasses is focussed on their high refractive index, high phonon energy, which enlarges the transmission infrared spectra range up to ∼6 μm, and an excellent non-linear behaviour.[5] These properties, due to the high polarisability of Te^{4+}-ions (with a solitary electron pair $5s^2$), can be even more enhanced by means of the incorporation of other heavy metals oxides that can be easily polarised (e.g. Bi^{3+}, Pb^{2+}) or with empty d orbital (Ti^{4+}, Nb^{5+}).[5] Apart from these special optical properties, other advantages of such glasses are their good thermal and chemical stability, low tendency to crystallisation and their ability to host rare earth ions. This fact has allowed the preparation of several glass families with added interest in optical and electrooptical applications and with noticeable advantages, in comparison with other conventional glasses. Kim et al.[6,7] studied non-linear optical properties of several systems of binary tellurite glasses, Charton et al.[8] determined the structural characteristics of glasses in the TeO_2–WO_3 system, Tokuda et al.[9] prepared waveguides into Nb_2O_5–TeO_2 glasses. Other authors have enlarged the field of knowledge about tellurite glasses with research concerning ternary and quaternary systems.[10–22]

The aim of the present work is to explore and to limit the glass forming area in the TeO_2–TiO_2–Nb_2O_5 system, as well as to characterise the structure of the glasses obtained and to determine some of their properties. Afterwards, some of such glasses will be selected as the best for a further study focussed on their application as photonic materials. Determination of the optical properties of these glasses will be the purpose for future research.

2. Experimental

2.1. Glasses composition and preparation

Twelve samples were prepared in the TeO_2–TiO_2–Nb_2O_5 system. Nominal compositions are summarised in Table 1.

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Table 1
Composition of the samples prepared (mol%) and density at 23 °C (g cm^{-3})

Sample	TeO_2	TiO_2	Nb_2O_5	Density
1	95	–	5	5.518
2[a]	95	5	–	Not determined
3	90	–	10	5.413
4	90	5	5	5.429
5	90	10	–	5.455
6	85	–	15	5.327
7	85	5	10	5.334
8	85	10	5	5.345
9[a]	85	15	–	5.361
10	80	5	15	5.241
11	80	10	10	5.255
12[b]	75	10	15	5.170

[a] Crystalline sample.
[b] Opal glass.

By melting 10 g batches of high-purity reagents TeO_2 (Alfa 99.99), Nb_2O_5 (Alfa 99.9985) and TiO_2 (Sigma Aldrich 99.99), the selected compositions were prepared by heating them in a platinum crucible placed in an electrical vertical furnace Thermostar^{TM}, at variable temperatures between 720 and 840 °C during 30 min. The melts were stirred three times and then poured onto a preheated brass plate, annealed 15 min at 400–440 °C and further cooled at 3 °C min^{-1} down to room temperature. All the samples prepared are undoubtedly transparent glasses, except sample nos. 2, 9 and 12.

2.2. Characterisation techniques

FT infrared spectra were recorded with a Nicolet^{TM} model Magna 550 spectrophotometer in the 1100–400 cm^{-1} range, by using the CsI pellets technique. 0.0005 g of each sample were diluted in 0.1000 g anhydrous CsI and pressed up to 10 tonnes. Spectra were immediately recorded. The densities were determined at 23 °C by the Archimedes' method dipping the samples of the investigated glasses in trichloroethylene ($d_{23\,°C}$ = 1.455 g cm^{-3}). The experimental density data obtained as well as the other values calculated from them are affected by a maximum error of 0.04%.

Glass transition temperature T_g and linear expansion coefficient $\alpha_{100–320\,°C}$ were determined with a differential dilatometer Netzsch^{TM}, model 402 P. For this purpose, planoparallel slabs of the samples were cut and polished by the two sides in which the palpator system of the equipment was placed. Experimental T_g values obtained are affected by a maximum error of 1%, while the experimental values of α are affected by a maximum error of 0.4%.

From optically polished planoparallel slabs 1 mm thickness optical absorption spectra were obtained in the 300–900 nm range. A spectrophotometer Shimadzu^{TM} model 3100 was used. Only transparent glass samples were optically studied. Those samples were cut and polished firstly using a 600 grit SiC paper and then with CeO_2 aqueous suspension.

Crystalline phases in the samples prepared were identified by X-ray diffraction. A Philips^{TM} X Pert diffractometer was used under the following experimental conditions: Cu Kα_1 radiation (λ = 0.15405 nm) with a Ni filter and a 0.1 mm detector collimator at 50 kV and 40 mA.

3. Results and discussion

3.1. Glass forming area

Fig. 1 shows the compositions studied in the ternary TeO_2–TiO_2–Nb_2O_5 system as well as the glass forming region. Among the compositions in the binary TeO_2–TiO_2 system, only the sample $90TeO_2 \cdot 10TiO_2$ could be obtained as a glass. Increasing the TeO_2 molar percentage up to the composition $95TeO_2 \cdot 5TiO_2$ enhanced the formation of α-TeO_2. Consequently, decreasing the TeO_2 molar percentage up to 85% (sample $85TeO_2 \cdot 15TiO_2$) caused a mixture of crystalline tetragonal α-TeO_2 and cubic $TiO_2 \cdot 3TeO_2$, as was confirmed by XRD. In the binary system, TeO_2–Nb_2O_5 the composition $85TeO_2 \cdot 15Nb_2O_5$ is the forming glass limit under the experimental conditions used in the present work. Nevertheless, the glass forming region can be enlarged by using other preparation conditions.[23] All the other compositions prepared yielded lightly yellow transparent glasses, unless the sample $75TeO_2 \cdot 10TiO_2 \cdot 15Nb_2O_5$ which originated an opal glass.

3.2. FTIR spectra

The FTIR spectra of the glasses of the present investigation are shown in Fig. 2. As known, tellurite glasses follow the pattern of crystalline α-TeO_2, which are formed by [TeO_4] groups as trigonal bipyramids (tbp).[17] In tellurite glasses, such structural units can progressively form [TeO_{3+1}] and trigonal pyramids [TeO_3] (tp) when the glass network becomes more open and non-bridging oxygens are created due to the incorporation of modifier ions.[17,24–26]

The spectrum of crystalline TeO_2 (Fig. 2a) shows two net peaks at 775 and 658 cm^{-1} and a shoulder at about 627 cm^{-1}.

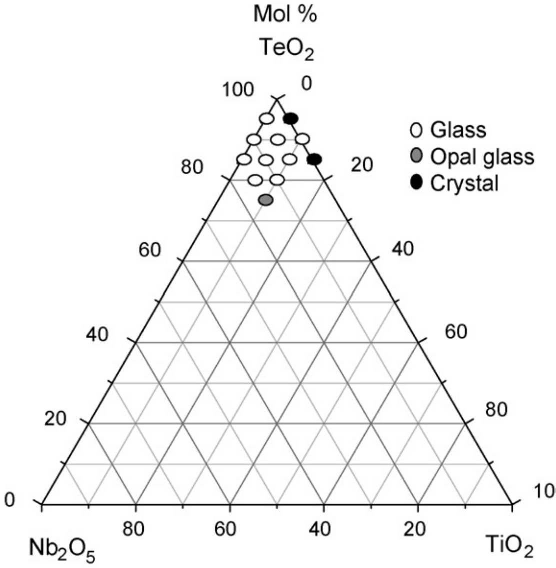

Fig. 1. Glass forming region in the TeO_2–TiO_2–Nb_2O_5 ternary system.

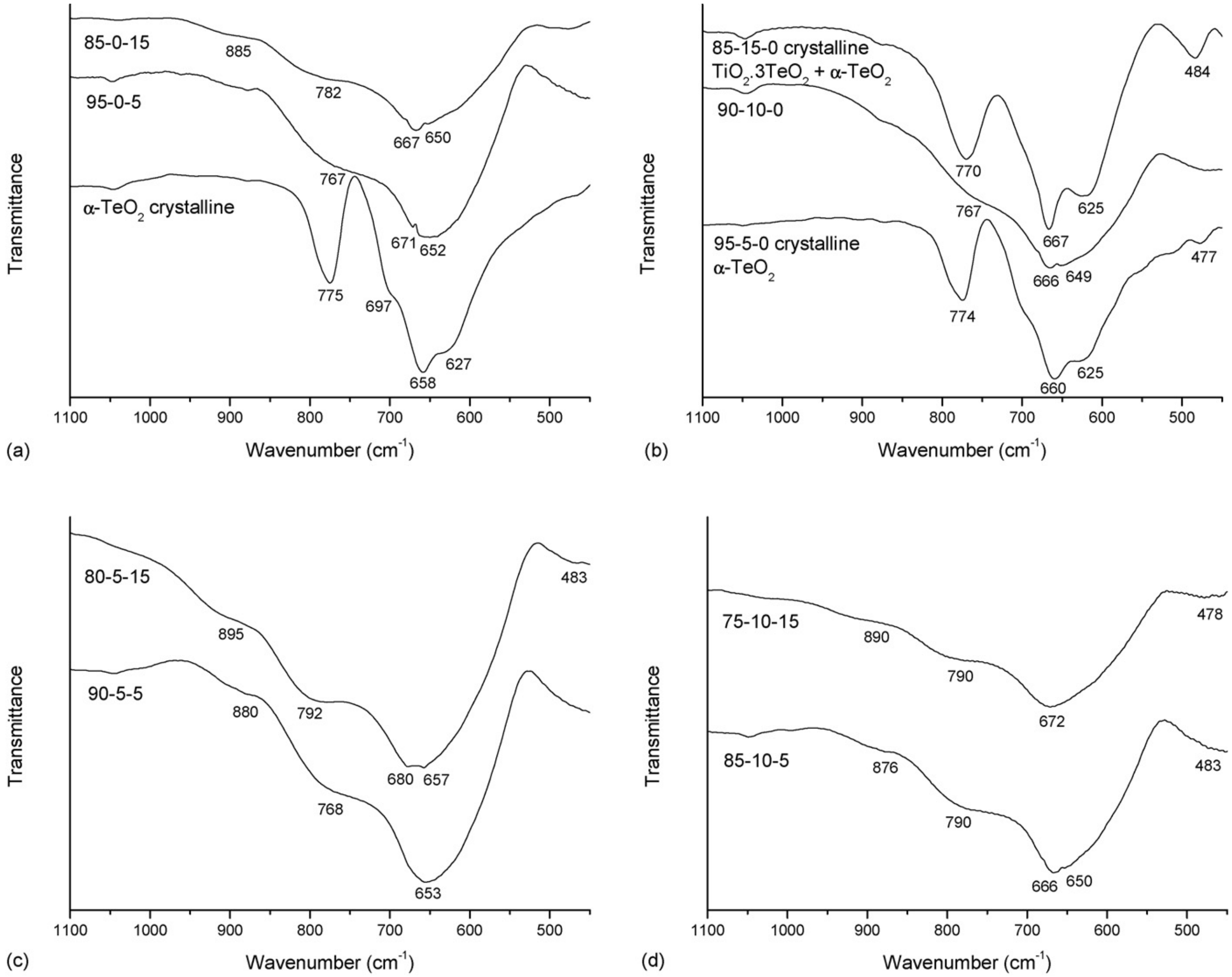

Fig. 2. FTIR spectra of some of the samples studied: (a) binary TeO_2–Nb_2O_5 samples; (b) binary TeO_2–TiO_2 samples; (c) ternary 5 mol% TiO_2 samples; (d) ternary 10 mol% TiO_2 samples.

3.2.1. Glasses in the binary TeO_2–Nb_2O_5 system

The incorporation of Nb_2O_5 causes an important change in the tellurite glassy network. Two characteristic bands of the $[TeO_4]$ (tbp) groups in α-TeO_2 at 627 and 658 cm^{-1} appear together forming a wide band at about 652–671 cm^{-1} for the glass $95TeO_2{\cdot}5Nb_2O_5$, while for the glass $85TeO_2{\cdot}15Nb_2O_5$ such vibration appears at about 650–667 cm^{-1}. This band contains the sharp absorption peak at 620 cm^{-1}, which is observed in potassium niobate glasses and was assigned by Sato et al.[27] to the Nb–O stretching, in $[NbO_6]$ octahedral groups linked by their vertices. The TeO_2 band at 775 cm^{-1} forms a shoulder centred at 767 and 782 cm^{-1}, respectively (Fig. 2a).

The shift of the mentioned bands can be explained by a change of the coordination of Te atoms in $[TeO_4]$ (tbp) groups towards $[TeO_3]$ (tp) groups, due to the fact that Te–O bonds in $[TeO_3]$ polyhedra are shorter and, hence, less polarised. This structural change, which occurs when modifier ions are incorporated (as Wen-Hai et al.[10] pointed out in PbO–Nb_2O_5–TeO_2 glasses, Arnaudov et al.[26] in binary TeO_2–Nb_2O_5 glasses and Lin et al.[18] in TeO_2–Nb_2O_5–ZnO) confirms that in the glasses studied here most of the Nb^{5+}-ions are partially incorporated to the glassy TeO_2 network as modifier ions in $[NbO_6]$ groups. This yields the formation of non-bridging oxygens and the shortening of the Te–O bond, which reinforces its vibration.

To support this interpretation let us indicate that by each TeO_2 mole that is substituted by 1 mol of Nb_2O_5, two Nb^{5+}-ions and five oxygen ions are incorporated to the network. That is, the oxygen excess is not enough to form the coordination of $[NbO_6]$ groups. To complete this kind of coordination the incorporation of oxygen atoms from the $[TeO_4]$ groups is required with the subsequent partial formation of $[TeO_3]$ groups.

Although Lin et al.[18] assume a network forming role for niobium oxide and they assign to the $[NbO_4]$ vibrations the band at 890 cm^{-1} in TeO_2–Nb_2O_5–ZnO glasses, the niobium oxide incorporation in the glasses studied here as $[NbO_4]$ groups is not probable. If $[NbO_4]$ groups would exist, the ratio $[TeO_3]/[TeO_4]$ will change since the formation of such niobium tetrahedral groups will contribute to restore bridging bonds and will increase the number of [TeO_4] (tbp) groups just diminishing the [TeO_3] (tp) groups. In that case a shift of the [TeO_4] characteristic bands towards its initial position at lower wavenumbers would be observed, as Murugan et al.[22] pointed out in its Raman study on glasses containing a maximum Nb_2O_5 content of the same order of magnitude. In our opinion, this band that appears as a shoulder at ∼880 cm^{-1} in binary and ternary tellurite glasses containing Nb_2O_5 (Fig. 2a, c and d), confirms the existence of [NbO_6] octahedral groups, as Tatsumisago et al.[28] described for ternary lithium–earth alkaline niobate glasses.

3.2.2. Glasses in the binary TeO_2–TiO_2 system

The FTIR spectrum of the sample $95TeO_2 \cdot 5TiO_2$ (Fig. 2b), whose X-ray diffractogram (not shown) corresponds to that of the crystalline tetragonal α-TeO_2, does not show any noticeable difference when compared with the spectrum of the reference crystalline TeO_2. The presence of 5 mol% TiO_2 does not change the spectrum, except the appearance of a small band at 477 cm^{-1}. The spectrum of the glass $90TeO_2 \cdot 10TiO_2$ also shows a shift of the bands at 625 and 660 cm^{-1} towards 649 and 666 cm^{-1}, respectively (similar behaviour as the glasses of the TeO_2–Nb_2O_5 binary system), giving rise to a wide band, which includes the band at 774 cm^{-1} as a shoulder. This widening can be attributed to a deformation of [TeO_4] groups, due to the incorporation of TiO_2. The molar substitution of TeO_2 by TiO_2, which show the same number of oxygens, does not vary the oxygen/cation ratio in the resulting network. The spectrum of the sample $85TeO_2 \cdot 15TiO_2$ which is formed by two crystalline phases (α-TeO_2 and $TiO_2 \cdot 3TeO_2$) is similar to that of α-TeO_2. The only difference is the more intense and better defined band at 484 cm^{-1}, which corresponds to the small vibration at 477 cm^{-1} pertaining to binary glasses containing 5 and 10% TiO_2. Such a band can be attributed to the Ti–O vibration in octahedral [TiO_6] groups that usually appears in silicatitanate glasses in the 500–600 cm^{-1} range.[29,30] The lower field intensity of Te^{4+}-ions in tellurite glasses related to the field intensity of Si^{4+}-ions in silicate glasses, probably causes the shift observed around ∼500 cm^{-1} in silicate glasses towards ∼480 cm^{-1} in tellurite glasses.

A comparison between the structural variations of the tellurite network induced by the incorporation of 5 mol% TiO_2 with those produced by the same molar percentage of Nb_2O_5 (bearing in mind that for each mole of TiO_2, two Nb^{5+}-ions are incorporated), indicates that the main difference that can be observed between the two binary samples $95TeO_2 \cdot 5TiO_2$ and $95TeO_2 \cdot 5Nb_2O_5$ is that the former is not a glass (indeed it is formed by crystalline TeO_2 and a low TiO_2 concentration, which does not affect the corresponding spectrum), and in the latter one the adding of Nb_2O_5 favours the glass formation with the small network distortion already described.

3.2.3. Glasses in the ternary TeO_2–TiO_2–Nb_2O_5 system

In the two series of ternary glasses with constant content of 5 and 10 mol% TiO_2 (Fig. 2c and d) the increasing incorporation of Nb_2O_5 from 5 to 15 mol% causes a progressive shift of the TeO_2 characteristic bands, especially for that at 774 cm^{-1}, which appears at about 790–792 cm^{-1}. This shift is even higher than the shift observed between 756 and 778 cm^{-1} in the samples of the TeO_2–Nb_2O_5 binary system for the same molar variation from 5 to 15% Nb_2O_5. In other words, Te–O bonds are reinforced as a consequence of the simultaneous presence of Ti^{4+}-ions and Nb^{5+}-ions, which confirm their role as modifier ions.

3.3. Density and molar volume

The measured density values listed in Table 1 vary between 5.170 and $5.518 \pm 2 \times 10^{-3}$ g cm^{-3} for the glasses $75TeO_2 \cdot 10TiO_2 \cdot 15Nb_2O_5$ and $95TeO_2 \cdot 5Nb_2O_5$, respectively. From these density values, the molar volume of glasses ($V_M = \Sigma x_i M_i/\rho$) and the molar volume of oxygen (volume of glass in which 1 mol of oxygen is contained, $V_O = (\Sigma x_i M_i/\rho)(1/\Sigma x_i n_i)$) were calculated. x_i is the molar fraction of each component i, M_i the molecular weight, ρ the glass density and n_i is the number of oxygen atoms in each oxide.

3.3.1. Molar volume

As seen in Fig. 3, the variation of the molar volume of the glasses is plotted as a function of the molar fraction of each one of the three oxides and a series of straight lines are obtained. Among the three oxides, the most important one in contributing to the increase in the molar volume is the Nb_2O_5 (Fig. 3a), since for each mole incorporated, two niobium atoms and five oxygen atoms are introduced, while for the other two components the cation/oxygen ratio is 1/2. For the same Nb_2O_5 concentration the molar volume increases with the TeO_2 content and decreases with the TiO_2 content. Increasing the molar fraction of TiO_2, the molar volume decreases with higher slope when TiO_2 substitutes the Nb_2O_5 mole by mole. However, when the TiO_2 substitutes the TeO_2, the molar volume scarcely changes, as can be observed in the three lines (almost parallel with slopes -5.5 ± 0.2) of Fig. 3b. The molar volume decreases strongly when the TeO_2 substitutes the Nb_2O_5 (lines with an average slope of -36.5 ± 0.6) and slightly increases when it substitutes the TiO_2 (lines with slope of 5.5 ± 0.2) (Fig. 3c).

Molar volume is limited by the space occupied by the structural units of the three oxides forming 1 mol glass. Logically, the molar volume increases: (i) with the number of oxygen atoms; (ii) with the proportion and cation radius; (iii) when the coordination number increases and (iv) when the field intensity of cations diminishes.

Therefore, for the same molar percentage of oxide, the Nb_2O_5 contributes to increase the glass molar volume more than the other two oxides. This is due to its octahedral coordination with the highest number of oxygen atoms per cation, which occupy a larger space. For constant TiO_2 concentration, the substitution of 10% TeO_2 by Nb_2O_5 mole by mole yields a molar volume increase of 11%. However, for constant Nb_2O_5 the substitution mole by mole of 10% TeO_2 by TiO_2 gives rise to a molar volume decreasing of 1.7%. This can be explained by the low space taken by the tetrahedral coordination of [TiO_4] groups, due to both the lower radius of Ti^{4+}-ions and their higher field intensity.

Since for glasses molar refraction and polarisability is directly proportional to the molar volume, one can predict that glasses with the higher molar volume will be those showing

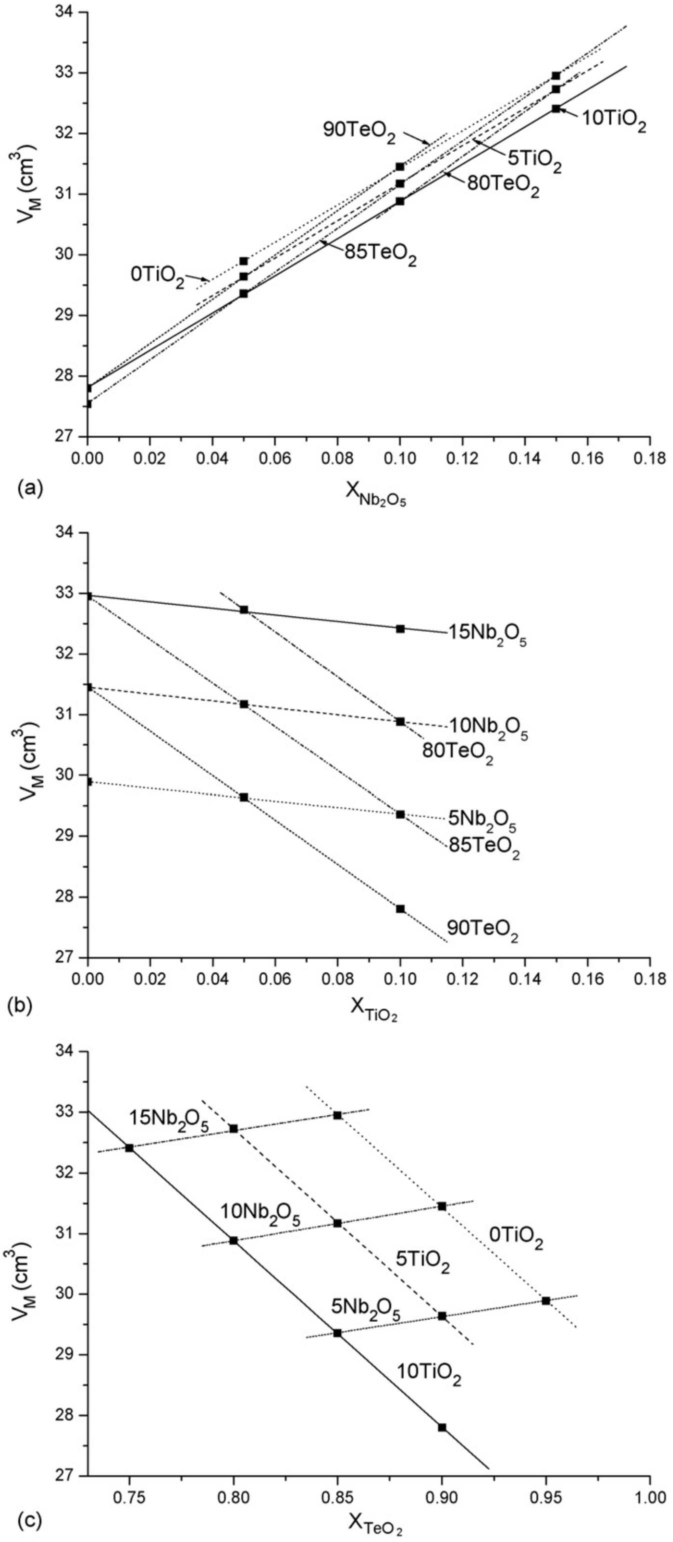

Fig. 3. Variation of the molar volume of glasses as a function of the molar fraction of each one of their component oxides: (a) Nb_2O_5, (b) TiO_2 and (c) TeO_2.

higher refractive index, lower phonon energy and higher third order dielectric susceptibility (χ^3).

3.3.2. Oxygen molar volume

The variation of the oxygen molar volume (V_O) has been studied as a function of the cation fraction (X_{cat}) for each one of the three components, for constant concentration of the other two components. This parameter has been referred as the ion fraction instead of the molar fraction. The reason is based on two factors: (i) because the cation/oxygen ratio is different for the three oxides of the glass system studied and (ii) because in this way the influence due to the cations is more clearly defined, since their polarising power (or their field intensity) is the determining factor for the structural packing of the oxygen-based glassy network.

The oxygen molar volume of glasses gives better information about their structure. Their variation as a function of the cation fraction shows a different behaviour compared with those of the molar volume previously described. As seen in Fig. 4a, the molar volume strongly increases with the molar fraction of Nb_2O_5, while the oxygen molar volume decreases as a function of the cation fraction $X_{Nb}{}^{5+}$, when the molar proportion of the other two components is constant.

The decreasing of the oxygen molar volume is a linear function and can be fitted to three lines almost parallel (slope -2.65 ± 0.8) for constant molar percentages of TiO_2, i.e. when the Nb_2O_5 substitutes the TeO_2 mole by mole. For the same $X_{Nb}{}^{5+}$, the molar volume decreases about 0.9% when 5 mol% TeO_2 is substituted by 5 mol% TiO_2. Such decreasing reaches 1.8% when 10 mol% TiO_2 is substituted by 10 mol% TeO_2. In Fig. 4a, it is also observed that for constant molar percentages of TeO_2, the V_O values decrease as a linear function with the fraction $X_{Nb}{}^{5+}$. In this case, three straight lines almost parallel can be fitted when Nb_2O_5 substitutes TiO_2, though such decreasing occurs with lower slope (-1.1 ± 0.25). That is, the oxygen molar volume V_O always decreases with the increasing of $X_{Nb}{}^{5+}$ both when Nb_2O_5 substitutes the TeO_2 and the TiO_2. Since this decreasing is more noticeable in the first case, for the same $X_{Nb}{}^{5+}$ the V_O is the lowest when the TiO_2 molar percentage is the highest and the TeO_2 molar percentage is the lowest.

The plot of V_O as a function of $X_{Ti}{}^{4+}$ shown in Fig. 4b confirms the former results. For constant molar percentages of Nb_2O_5, when TeO_2 is substituted by TiO_2, the V_O values decrease linearly following three parallel lines with a practically constant slope (-2.61 ± 0.17). For the same $X_{Ti}{}^{4+}$ such decrease is about 1.6% when 5 mol% TeO_2 is substituted by 5 mol% Nb_2O_5, and at about 3.2% when 10 mol% TeO_2 is substituted by 10 mol% Nb_2O_5. On the contrary, for constant TeO_2 molar percentages, V_O also increases linearly with $X_{Ti}{}^{4+}$, when Nb_2O_5 is substituted by TiO_2. These straight lines are symmetric with very similar slopes to the one mentioned above but with a positive value. Therefore, it can be deduced that for constant $X_{Ti}{}^{4+}$, the TeO_2 causes the oxygen molar volume to increase in the same extension than the decrease caused by the same molar percentage of Nb_2O_5. In other words, between the contribution of Nb_2O_5 and the contribution of

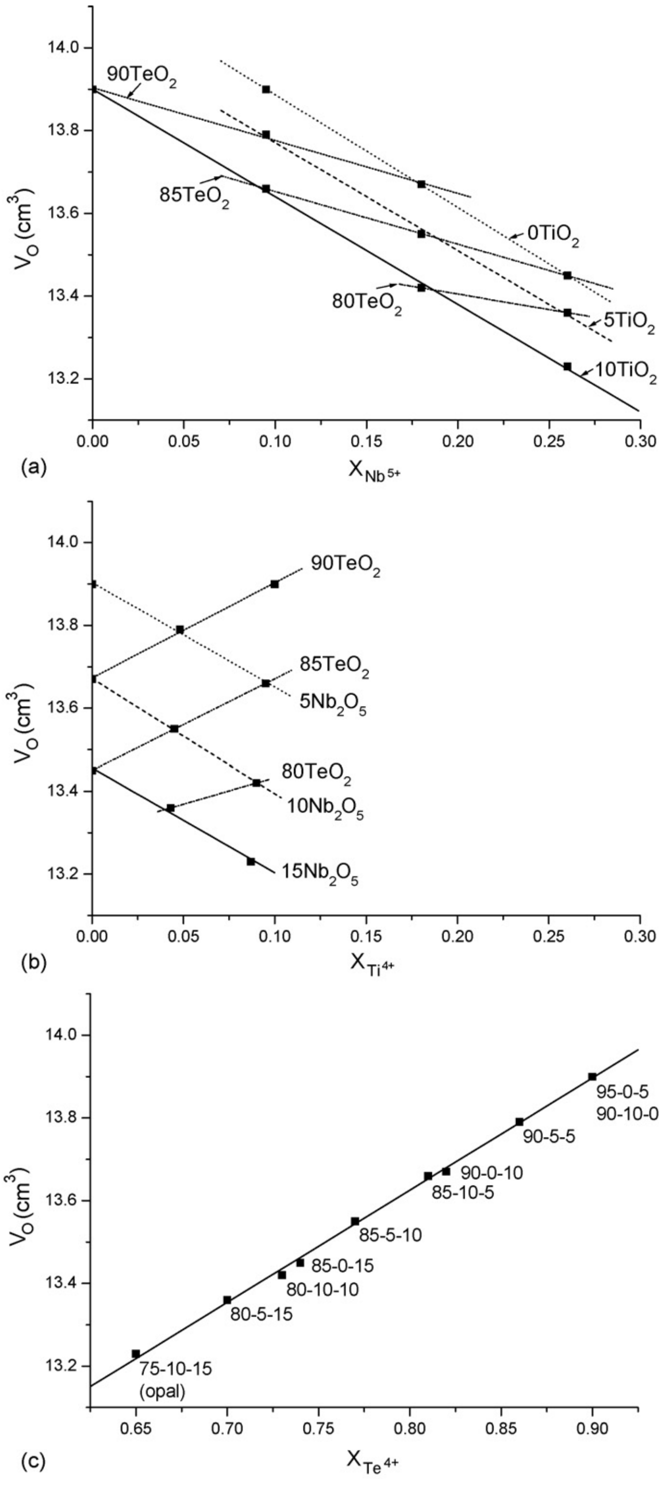

Fig. 4. Variation of the oxygen molar volume of glasses as a function of the cation fraction of each one of their component oxides: (a) Nb^{5+}, (b) Ti^{4+} and (c) Te^{4+}.

TeO_2, related the oxygen molar volume, there is a ratio of 1:2, approximately.

Fig. 4c shows how V_O increases linearly with $X_{Te}{}^{4+}$, independently of the molar percentages of the other two oxides. This indicates that TeO_2 is the most important constituent affecting the V_O value, since it is the major glass component and, hence, the network forming oxide.

The decrease of oxygen molar volume indicates structural packing in the glass network, which depends on two main factors: the cation radius and, especially, their field intensity. Therefore, the packing degree will be higher for higher cation field intensity and lower cation radius. In this way, it could be explained that both Nb^{5+} and Ti^{4+}, with the same field intensity (∼1.20), contribute in the same extent to reduce the oxygen molar volume. This also explains that the slopes of straight lines for constant molar concentrations [Nb_2O_5] and [TiO_2] are similar (-2.61 ± 0.18 and -2.65 ± 0.80, respectively) (Figs. 4a and b). On the contrary, Te^{4+}-ions, whose field intensity is the lowest (∼0.93), expand the glass network and increase the V_O value (Fig. 4c). This figure represents another confirmation about the same effect of both Ti^{4+}-ions and Nb^{5+}-ions on the V_O value when they substitute each other mole by mole. This also explains that segments corresponding to different constant concentrations of TiO_2 and Nb_2O_5 are located on the same straight line.

3.4. *Glass transition temperature*

In all cases, glass transition temperature T_g shows a linear variation when is plotted against the cation fraction of each one of the three components (Fig. 5). T_g values increase with $X_{Nb}{}^{5+}$ (Fig. 5a), and for constant values of $X_{Nb}{}^{5+}$, the glass transition temperature increases with the molar percentage of TiO_2 when it substitutes TeO_2. In the glass series with 80 mol% TeO_2 transition temperature does not change practically. For the two series with 85 and 90 mol% TeO_2 transition temperature lightly increases when TiO_2 is substituted by Nb_2O_5.

Likewise, Fig. 5b shows a series of straight lines indicating that T_g increases gradually with the cation percentage $X_{Ti}{}^{4+}$ when TeO_2 is substituted mole by mole by TiO_2 while the Nb_2O_5 concentration is constant. For the same $X_{Ti}{}^{4+}$ value, the lower is the TeO_2 molar content and the higher is the Nb_2O_5 concentration, the higher is the T_g increase. When $X_{Ti}{}^{4+}$ increases and the Nb_2O_5 concentration decreases under constant TeO_2 content, a clear T_g variation is not observed.

From these results, it can be deduced that as the proportion of Te^{4+}-former ions decreases, and consequently the glass network is open due to the higher number of non-bridging oxygens, the T_g values increase. This behaviour is the contrary respect to the currently observed in other glasses, since the incorporation of modifier ions causes a reticular broken down and a decreasing of the structural cohesion. These facts determine a drop of both T_g and softening temperature. This unusual behaviour in tellurite glasses can be explained on the basis of the FTIR spectra interpretation, i.e. on the progressive increasing of [TeO_3] (tp) groups which have stronger Te–O bonds, as a consequence of the increasing Nb^{5+}-modifier ions incorporation.

3.5. *Thermal expansion coefficient*

The values of thermal expansion coefficients $\alpha_{100\text{–}320\,^{\circ}\mathrm{C}}$ (Fig. 6) vary between 10.7 and $16.9 \times 10^{-6}\,K^{-1}$, following a monotonous behaviour. The lower expansion coefficient corresponds to the glass $80TeO_2{\cdot}5TiO_2{\cdot}15Nb_2O_5$, and the highest one to the glass $95TeO_2{\cdot}5Nb_2O_5$.

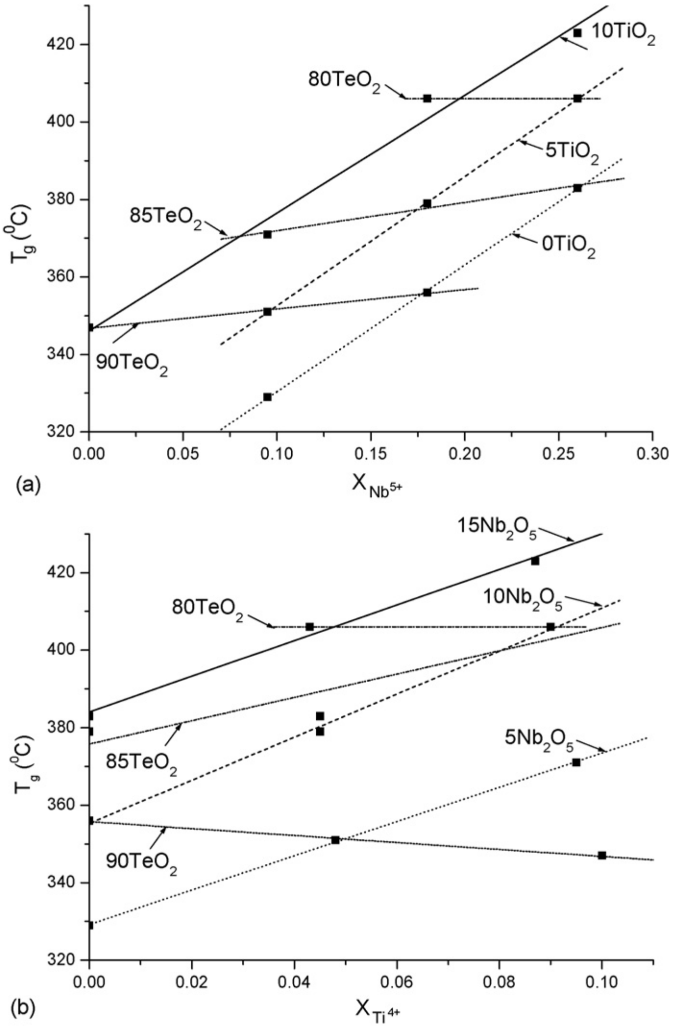

Fig. 5. Variation of the glass transition temperature T_g of glasses as a function of the cation fraction of their component oxides: (a) Nb^{5+} and (b) Ti^{4+}.

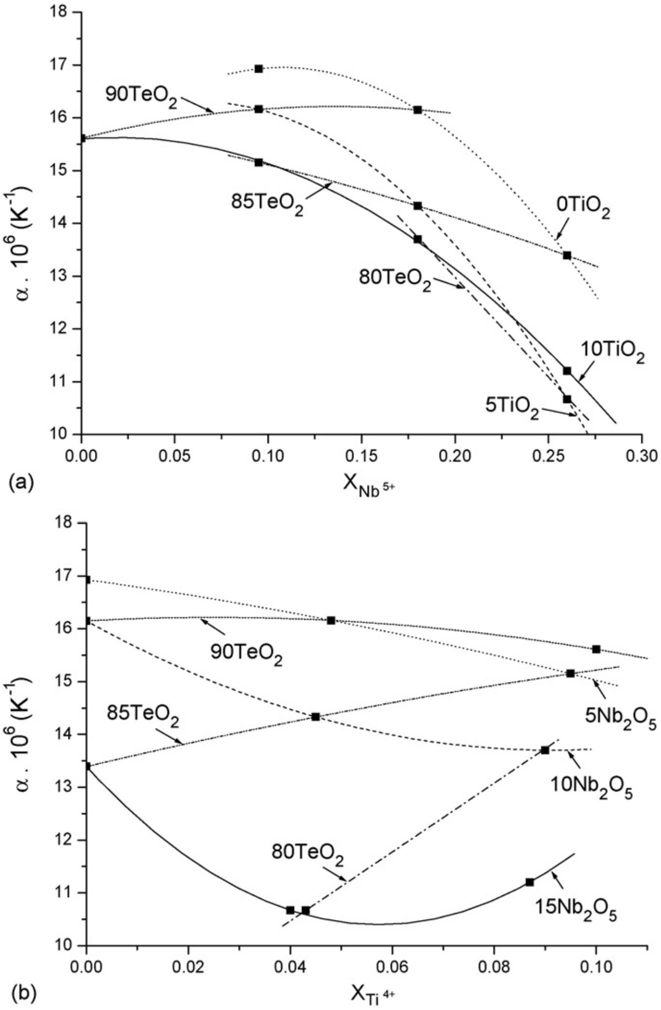

Fig. 6. Variation of the thermal expansion coefficient of glasses as a function of the cation fraction of their component oxides: (a) Nb^{5+} and (b) Ti^{4+}.

α Values decrease as the $X_{Nb}{}^{5+}$ increases when Nb_2O_5 substitutes TeO_2 mole by mole and the TiO_2 concentration remains constant (Fig. 6a). Such a decrease is more noticeable for molar concentrations of 5 and 10 mol% TiO_2. In glasses with a constant TeO_2 content (90, 85 or 80 mol%), the lower the TeO_2 content, the higher α variation as a function of $X_{Nb}{}^{5+}$. When [TiO_2] is substituted by [Nb_2O_5] mole by mole in the glass series with [TeO_2] = 80%, α varies suddenly. In the glass series with [TeO_2] = 85%, α decreases slightly. And, finally, in the glass series with [TeO_2] = 90%, α increases slightly.

Fig. 6b also shows a progressive α decrease with $X_{Ti}{}^{4+}$ when [Nb_2O_5] is constant and TeO_2 is substituted by TiO_2. On the contrary, the expansion coefficient increases with $X_{Ti}{}^{4+}$ when [Nb_2O_5] is substituted by [TiO_2] under constant [TeO_2]. α Values increase with the TeO_2 molar percentage, although the corresponding increasing slope decreases when the TeO_2 proportion increases. This behaviour (also attributable to the formation of [TeO_3] (tp) groups) is consistent with the transition temperature variation. As the $X_{Nb}{}^{5+}$ increases, T_g is raised up and α decreases as a consequence of the Te–O bonds reinforcement in the [TeO_3] groups. The substitution of [TeO_2] by [Nb_2O_5] under constant [TiO_2] causes a stronger α decreasing (high T_g increasing slope). When [TiO_2] is substituted by [Nb_2O_5] under constant [TeO_2], α decreasing is softer, and even shows a light increasing for [TeO_2] = 90%. In this case, the T_g increasing also proceeds with lower slope.

3.6. Optical absorption

It is well known that the UV absorption edge of the glasses shifts to longer wavelength by increasing the molecular weight of their components.[31–33] Liu et al.[31] observed in the BaO–TeO_2–B_2O_3 glass system that the absorption edge shifts from 320 towards 450 nm (E_g decreases), when the TeO_2 proportion increases from 15 to 60 mol%. Likewise, Ahmed et al.[32] also found a similar absorption edge shift in TeO_2–GeO_2 binary glasses when the molar ratio [TeO_2]/[GeO_2] increases. Moreover, Al-Ani et al.[33] observed in TeO_2–WO_3 binary glasses an absorption edge shift towards longer wavelength (lower E_g values), when the [TeO_2] is substituted by the [WO_3] heavier oxide.

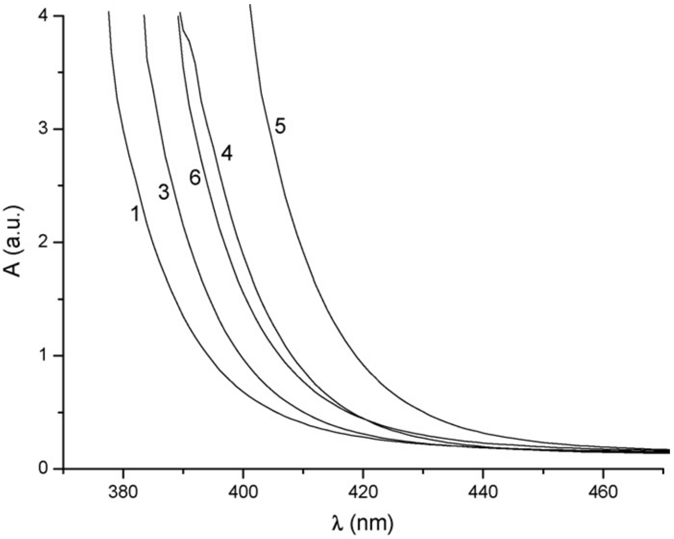

Fig. 7. Optical absorption spectra of some of the glass samples studied: glass 1, glass 3, glass 4, glass 5 and glass 6.

The absorption spectra of the glasses studied are plotted in Fig. 7. Such spectra were recorded from optically polished planoparallel glass slabs 1 mm thickness. For clarity only some spectra were represented: those from three samples with $[TeO_2] = 90$ mol%, and those of three samples with $[TiO_2] = 0$ and decreasing $[TeO_2]$ concentrations from 95 to 85 mol%. No absorption band in the 300–900 nm range is observed for all samples. The yellow colouring of the glasses is due to a variable shift of the ultraviolet absorption edge towards the visible range, which depends on the glass composition. In the same way as in the spectra after Liu et al.,[31] the absorption edge of the glasses studied here falls sharply to 400–450 nm and their base line is very straight. With the aim to calculate the absorption edge, the values corresponding to the same absorbance ($A = 0.5$) were conventionally taken. The glass energy gap E_g and its variation as a function of $X_{Te}{}^{4+}$ is shown in Fig. 8.

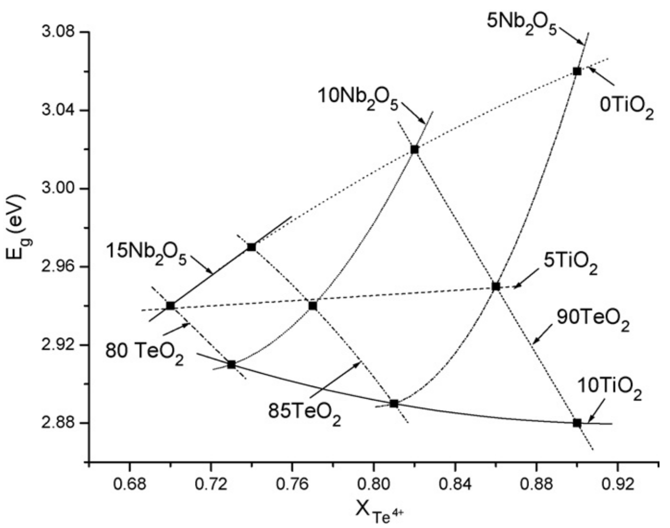

Fig. 8. Variation of the energy gap E_g referred to a constant optical absorbance ($A = 0.5$) as a function of the cation fraction $X_{Te}{}^{4+}$.

The highest value of E_g corresponds to the glass with higher molar proportion of TeO_2 (composition $95TeO_2{\cdot}5Nb_2O_5$) ($E_g = 3.06$ eV). For lower TeO_2 content, E_g progressively decreases when TeO_2 is substituted by TiO_2 for constant $[Nb_2O_5] = 5$ mol%, up to the composition $85TeO_2{\cdot}10TiO_2{\cdot}5Nb_2O_5$ ($E_g = 2.89$ eV). The higher the initial TeO_2 molar concentration, the higher the E_g decreasing. The increasing incorporation of TiO_2 is mainly responsible for the E_g diminishing. As is shown in Fig. 8, the line corresponding to $[TiO_2] = 0$ presents an increasing tendency against $X_{Te}{}^{4+}$; the $[TiO_2] = 5$ mol% line has a negligible slope and, finally, the $[TiO_2] = 10$ mol% shows a light decreasing tendency.

Likewise, when TeO_2 is substituted by Nb_2O_5 mole by mole, a strong E_g diminishing occurs for $[TiO_2] = 0$. This fact can be explained because the increasing incorporation of Nb^{5+}-ions as network modifiers open the network and creates non-bridging oxygens, as it was mentioned above. In the glass series with constant $[TiO_2] = 5$ mol%, the replacement of TeO_2 by Nb_2O_5 does not vary E_g practically. In the series with $[TiO_2] = 10$ mol%, the E_g value even decreases when TeO_2 is substituted by Nb_2O_5. This change of tendency is due to the TiO_2 incorporation, which affects the E_g value even more than the other two glass oxides.

When $[TeO_2]$ remains constant, the replacement of Nb_2O_5 by TiO_2 determines an E_g decreasing, which diminishes for lower $[TeO_2]$. The lowest E_g value (2.88 eV) corresponds to the glass $90TeO_2{\cdot}10TiO_2$.

Taking in mind these results, the present authors do not discard that Ti^{4+} could have a role as network modifier ions that, as is known, decrease the E_g value.

4. Conclusions

In the studied glasses the network is built by $[TeO_4]$ (tbp) groups. Nb^{5+}-ions play as network modifiers in octahedral coordination. They produce a noticeable glass network distortion as the TeO_2 characteristic FTIR absorption bands shift towards higher wavenumber indicate. Ti^{4+}-ions seem to be incorporated also as network modifiers in octahedral coordination as the $\sim 475\ cm^{-1}$ FTIR absorption band show (although for TiO_2 concentration as low as that of the glasses studied here, no network distortion occurs, compared with those produced by Nb^{5+}-ions). Both Ti^{4+}-ions and Nb^{5+}-ions contribute to a shift increasing of the characteristic TeO_2 FTIR absorption bands towards longer wavenumber. In all cases the TeO_2 structure based on trigonal bipyramids of $[TeO_4]$ (tbp) groups is maintained. Nevertheless, such a structure progressively changes to $[TeO_3]$ (tp) groups as the content of network modifiers increases.

The glasses molar volume strongly increases as a function of Nb_2O_5 molar fraction and slightly decreases when the TiO_2 molar fraction increases.

The oxygen molar volume increases when (i) TiO_2 is substituted by TeO_2 mole by mole under constant $X_{Nb}{}^{5+}$; (ii) when Nb_2O_5 is substituted by TeO_2 under constant $X_{Ti}{}^{4+}$ and (iii) when Nb_2O_5 is substituted by TiO_2 under constant $X_{Te}{}^{4+}$. The contribution of the three ions to the increase of the oxygen molar volume is in the order: $Te^{4+} > Ti^{4+} > Nb^{5+}$.

TiO_2 incorporation (and even more Nb_2O_5 incorporation) causes an improvement of the glasses thermal stability and a network reinforcement, which is pointed out by the T_g increasing and the α decreasing.

In glasses with a constant TeO_2 molar concentration the energy gap value E_g decreases when Nb_2O_5 is substituted by TiO_2 mole by mole. The lowest value corresponds to the glass $90TeO_2 \cdot 10TiO_2$.

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