



New glasses within the $\text{Tl}_2\text{O}-\text{Ag}_2\text{O}-\text{TeO}_2$ system: Thermal characteristics, Raman spectra and structural properties

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ABSTRACT

Within the $\text{Tl}_2\text{O}-\text{Ag}_2\text{O}-\text{TeO}_2$ system, a large glass-forming domain was evidenced and is presented for the first time. Densities, glass transition (T_g) and crystallization (T_c) temperatures of the relevant glasses were measured. A structural approach of these glasses as functions of the composition was performed using Raman scattering. The Raman spectra were analysed in terms of the structural modifications induced by the Tl_2O and Ag_2O modifiers. It has clearly evidenced a phase separation inherent in tellurite glasses with low valence cations (as Tl^+ and Ag^+). The glasses would be constituted of two phases only: one of pure TeO_2 and one of pure ortho-tellurite M_2TeO_3 ($\text{M} = \text{Ag}, \text{Tl}$) with the statistically mixed Ag–Tl cationic composition.

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1. Introduction

Tellurium dioxide-based glasses are currently considered as promising materials for nonlinear optical applications. They have various advantageous properties as malleability, homogeneity in a wide range of composition, chemical stability, weak absorption coefficients, high linear and nonlinear refractive indices and a large transparency window which spreads from the visible to the infrared region out to $7\ \mu\text{m}$ [1]. Therefore, some substantial literature has been devoted to the studies of such glasses during the last decade. Many binary and ternary phase diagrams were investigated and the existence of large glass-forming domains was evidenced for most of them [1].

The nature of the aforementioned optical properties of TeO_2 -based glasses is of special interest regarding both fundamental science and applied aspects. Numerous attempts were made to clarify the role of the structural constitution in those properties [2,3]. In our laboratory, extensive studies of TeO_2 glassy and crystalline phases were undertaken during the last 10 years including the lattice-dynamical analysis of the α , β , and γ - TeO_2

lattices [4–7]. Thus, it was evidenced that γ - TeO_2 is the closest crystalline structure to pure TeO_2 glass [7,8].

The ab-initio-theory-based studies unequivocally indicate an exceptionally high nonlinear susceptibility value of pure TeO_2 glass ($19.68\ (10^{-21}\ \text{m}^2/\text{V}^2)$). This peculiarity should be attributed to a strong delocalization of the electronic dielectric response occurring within polymerized $-\text{Te}-\text{O}-\text{Te}-$ chains rather than to the local polarization of a lone electronic pair related to the 5s orbital of tellurium atoms as customarily proclaimed [3,9].

Of a series of $\text{TeO}_2-\text{M}_n\text{O}_k$ binary systems systematically investigated at the SPCTS laboratory, a special attention was paid to the case $\text{M} = \text{Tl}$. The phase diagrams were obtained and analyzed under equilibrium and non-equilibrium conditions, and a large glassy domain was found. Three stable (Tl_2TeO_3 , α - $\text{Tl}_2\text{Te}_2\text{O}_5$, $\text{Tl}_2\text{Te}_3\text{O}_7$) and one metastable (β - $\text{Tl}_2\text{Te}_2\text{O}_5$) crystalline compounds [10–12] were revealed and their structures determined. The existence of a high-temperature polymorph of Tl_2TeO_3 was recently evidenced in [13].

The central points of these investigations were the nonlinear optical properties of the thallium tellurite glasses. Thus it was found that:

- (i) their third-order nonlinear susceptibility coefficient can be 50–100 times higher than that of SiO_2 ;
- (ii) such value tends to increase upon Tl_2O component addition (about $480 \times 10^{-23}\ \text{m}^2/\text{V}^2$, measured at $0.8\ \mu\text{m}$) [14,15]. This

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effect is not ordinary. Actually, as a rule, the addition of a modifier causes the TeO_2 framework to depolymerize into island-type isolated complex anions $[\text{Te}_n\text{O}_m]^{2(m-2n)-}$, thus decreasing the susceptibility value [16]. Exceptions to this rule are the glasses in which the modifier contains highly polarisable cations, in particular Tl^+ [15];

(iii) the Raman gain coefficient of the glasses can be up to 58 times that of a standard Corning 7980-2F fused silica [17].

However, TeO_2 - Tl_2O glasses materials were found relatively brittle and characterized by a low thermal stability. To overcome this drawback, maintain the good non-linear characteristics of the glasses, and even enlarge the scope of their interesting optical properties, the Tl_2O - M_xO_y - TeO_2 ternary systems were recently investigated at our laboratory. In particular, quite satisfactory results relating the thermo-mechanical stability were achieved by adding TiO_2 to thallium tellurite system [18].

Our last activity in that field concerns the influence of the Ag_2O modifier introduced into Tl_2O - TeO_2 glasses. Indeed, according to previous reports on silver-doped phosphate glasses [19], it is expected that Tl_2O - Ag_2O - TeO_2 glasses would show some interesting photoluminescent properties (without losing their initial high non-linearity), resulting from the presence of silver cations.

Some results of structural studies of silver tellurite glasses and of some metal-oxide silver tellurite ternary glasses have been already published [1,20–22]. More or less large glassy domains were found with respect to the melting and quenching conditions. In particular, a glassy domain was revealed in a range 0–46 mol% $\text{AgO}_{0.5}$ in Ref. [21]. In analyzing neutron diffraction and Raman spectra data, the authors concluded that a progressive depolymerisation of the TeO_2 glass structure occurs with increasing modifier oxides content. This depolymerisation is characterized by the transformation of the TeO_4 disphenoids into TeO_3 units [20–22]. Such a structural change is a trivial fact for M_xO_y - TeO_2 glasses [11]. One of the rare exceptions is the case $\text{M} = \text{Ti}$ for which the Ti-O bond distances in the glassy structure are very close to the Te-O ones. Consequently, the Te-O-Te bridges are just replaced by Te-O-Ti ones and the glass framework is conserved [18].

A stable silver tellurite crystalline phase was detected in the Ag_2O - TeO_2 phase diagram, Ag_2TeO_3 [23]. This phase exists in two polymorphic forms, a metastable orthorhombic form which transforms irreversibly into the monoclinic stable variety above 573 K [24].

To the best of our knowledge, no crystalline compound and no glass have been evidenced within the binary Ag_2O - Tl_2O system. We can only indicate some investigations of ternary systems (see e.g., the study of silver-thallium borate glasses [25]).

Our present work was initially aimed at the determination of the glass formation domain within the Tl_2O - Ag_2O - TeO_2 ternary system which has never been explored. Then, the thermal behaviour of the glasses including the measurements of the glass-transition (T_g) and crystallization (T_c) temperatures was studied and the evolution of the glassy structure with increasing modifier component was analysed by using Raman spectroscopy. The results obtained are presented and discussed in this paper.

2. Experimental

Glassy samples were prepared by first melting at 800 °C in air for 15 min in platinum crucibles intimate mixtures of high purity Tl_2CO_3 (Aldrich, 99.9%), Ag_2O (99.9%) and home-made TeO_2 . The former was prepared by decomposition, at 550 °C, of commercial H_6TeO_6 (Aldrich, 99.9%). The decomposition of Tl_2CO_3 (CO_2 evaporation) was ensured during the melting. The melts (2 g for the bulk samples and 200 mg for the powder samples) were then fast-quenched in a freezing mixture consisting of ice, ethanol and

NaCl (temperature about -14 °C). Glass-forming region was determined by optical inspection of the obtained products (which were in the case of glassy samples transparent) and by using X-ray diffraction (D5000 Siemens diffractometer, Sol-X detector, $\text{Cu K}\alpha$ radiation, step size = 0.04°).

Glass transition (T_g) and crystallization (T_c) temperatures were measured by heat flux differential scanning calorimetry (Netzsch STA 409 apparatus). The powdered samples (~30 mg) were introduced into platinum crucibles and the DSC curves were recorded between 20 and 500 °C using a heating rate of 10 °C/min and under nitrogen atmosphere. The glass transition temperature was taken at the inflection point of the slope change of the calorimetric signal associated with this transition. The crystallization temperature was taken (when an exothermic peak was observed) at the intersection of the slope of this exothermic peak with the baseline. The densities of glassy samples were measured on finely ground powders by helium pycnometry (Accupyc 1330 pycnometer).

The Raman spectra of powder sample were recorded in the 80–1000 cm^{-1} range and in back-scattering mode at 514.532 nm using a T64000 Jobin-Yvon spectrophotometer operating in triple subtractive configuration (1800 grooves/mm) associated to a liquid nitrogen-cooled CCD detector. Measurements were performed at low power (<10 mW on the surface of the sample) of the excitation line, in order to avoid any damage of the glasses. The scattered light was collected through a microscope objective (50× LWD) and confocal filtering (0.1 mm). The spectral resolution was about 2.5 cm^{-1} at the exciting line. All samples were measured three times to check the reproducibility of spectra and to enhance the accuracy of the data by accumulation.

The Raman measurements of bulk sample were carried out on an inVia Reflex Raman spectrometer of the Renishaw Company at 514 nm. The spectra were recorded in a linefocus mode (in order to minimize the damage of the samples) centred to 500 cm^{-1} over a time of 1 s with the diffraction grating of 1800 grooves/mm (spectral resolution about 2.7 cm^{-1}). The laser power at the sample level and through an objective 50× was 20 mW.

3. Results and analysis

3.1. Glass formation

A large glass forming domain observed within the Tl_2O - Ag_2O - TeO_2 system is presented in Fig. 1. The glasses are all yellow, the

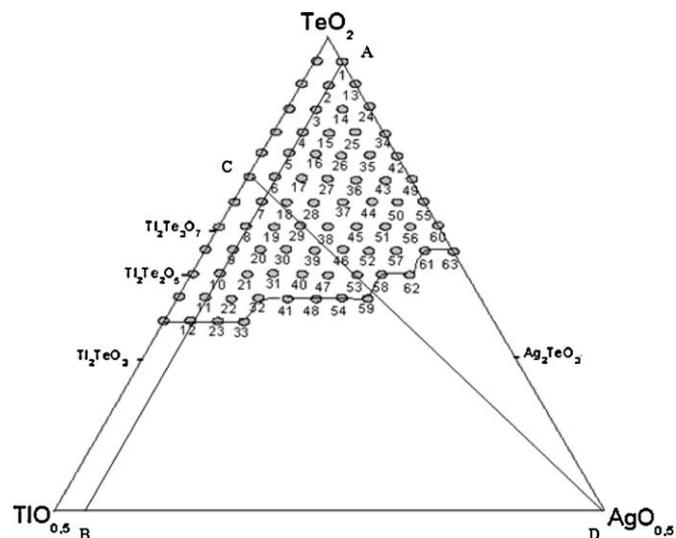


Fig. 1. Glass forming domain at 800 °C under ice-quenching conditions within the Tl_2O - Ag_2O - TeO_2 system.

intensity of the colour decreasing with increasing Ag₂O content. For rich-Ag₂O content the glasses become grey. Using such specific quenching conditions as freezing mixture of ice, ethanol and NaCl (temperature about -14 °C), the glass forming domain within the TeO₂-Ag₂O binary system was slightly enlarged (0–45 mol% AgO_{0.5}) with respect to those reported in the literature [1,20–22].

3.2. Thermal properties and densities of glasses

The thermal characteristics and density of some glasses are listed in Table 1. The samples are labelled as indicated in Fig. 1. The variation with the composition of the density, glass transition and crystallisation temperatures are shown in Fig. 2. The composition

Table 1
Glass-transition (T_g) and crystallisation (T_c) temperatures, thermal stability (T_c-T_g) and density of some glasses within the TeO₂-Tl₂O-Ag₂O system (the samples are numbered as labelled in Fig. 1).

No	Composition (mol%) TeO ₂ -TlO _{0.5} -AgO ₀	T_g (± 5 °C)	T_c (± 5 °C)	T_c-T_g (± 5 °C)	Density (± 0.05)
9	90-10-0	277	320	43	5.51
9	80-20-0	245	322	77	6.13
9	70-30-0	204	317	113	6.40
1	90-00-10	260	290	24	5.63
13	90-00-10	260	290	30	5.68
24	85-00-15	250	276	26	5.76
34	80-00-20	246	277	31	5.75
42	75-00-25	240	273	33	5.81
49	70-00-30	225	270	45	6.02
55	65-00-35	210	268	58	6.12
60	60-00-40	195	268	73	6.24
63	55-00-45	177	244	67	6.28
2	90-05-5	264	288	24	5.70
14	85-05-10	247	298	51	5.85
25	80-5-15	234	275	41	5.95
35	75-5-20	214	276	62	5.98
43	70-05-25	213	267	54	6.04
50	65-05-30	199	267	77	6.17
56	60-05-35	183	266	83	6.28
61	55-05-40	165	233	68	6.37
3	85-10-5	251	282	31	5.68
15	80-10-10	226	287	61	5.90
26	75-10-15	210	273	63	6.07
36	70-10-20	195	268	73	6.15
44	65-10-25	189	263	74	6.25
51	60-10-30	172	260	88	6.37
57	55-10-35	158	227	69	6.44
62	50-10-40	141	205	64	6.42
4	80-15-5	231	281	50	5.90
16	5-15-10	211	275	64	6.13
27	70-15-15	191	270	79	6.23
37	65-15-20	181	258	77	6.15
45	60-15-25	169	260	91	6.40
52	55-15-30	151	222	69	6.52
58	50-15-35	135	208	73	6.49
5	75-20-5	208	281	73	6.07
17	70-20-10	197	276	79	6.19
28	65-20-15	173	258	85	6.37
38	60-20-20	155	234	79	6.41
46	55-20-25	145	219	74	6.58
53	50-20-30	128	192	64	6.68
59	45-20-35	115	154	39	6.70
6	70-25-5	191	270	79	6.27
18	65-25-10	173	268	95	6.34
29	60-25-15	152	255	103	6.26
39	55-25-20	133	203	70	6.47
47	50-25-25	124	193	69	6.70
54	45-25-30	111	161	50	6.71
7	65-30-50	171	266	95	6.42
19	60-30-10	140	260	120	6.50
30	55-30-15	129	202	73	6.51
40	50-30-20	120	178	58	6.68
48	45-30-25	112	150	38	6.74
8	60-35-5	151	244	93	6.57
20	55-35-10	131	215	84	6.67
31	50-35-15	105	182	77	6.63
41	45-35-20	110	156	46	6.64
9	55-40-5	130	221	91	6.73
21	50-40-10	111	173	62	6.72
32	45-40-15	98	150	52	6.98
10	50-45-5	120	214	94	6.85
22	45-45-10	90	154	64	6.91
33	40-45-15	83	111	28	7.19
11	45-50-5	103	170	67	7.02
23	40-50-10	78	110	32	7.16
12	40-55-5	85	108	23	7.20

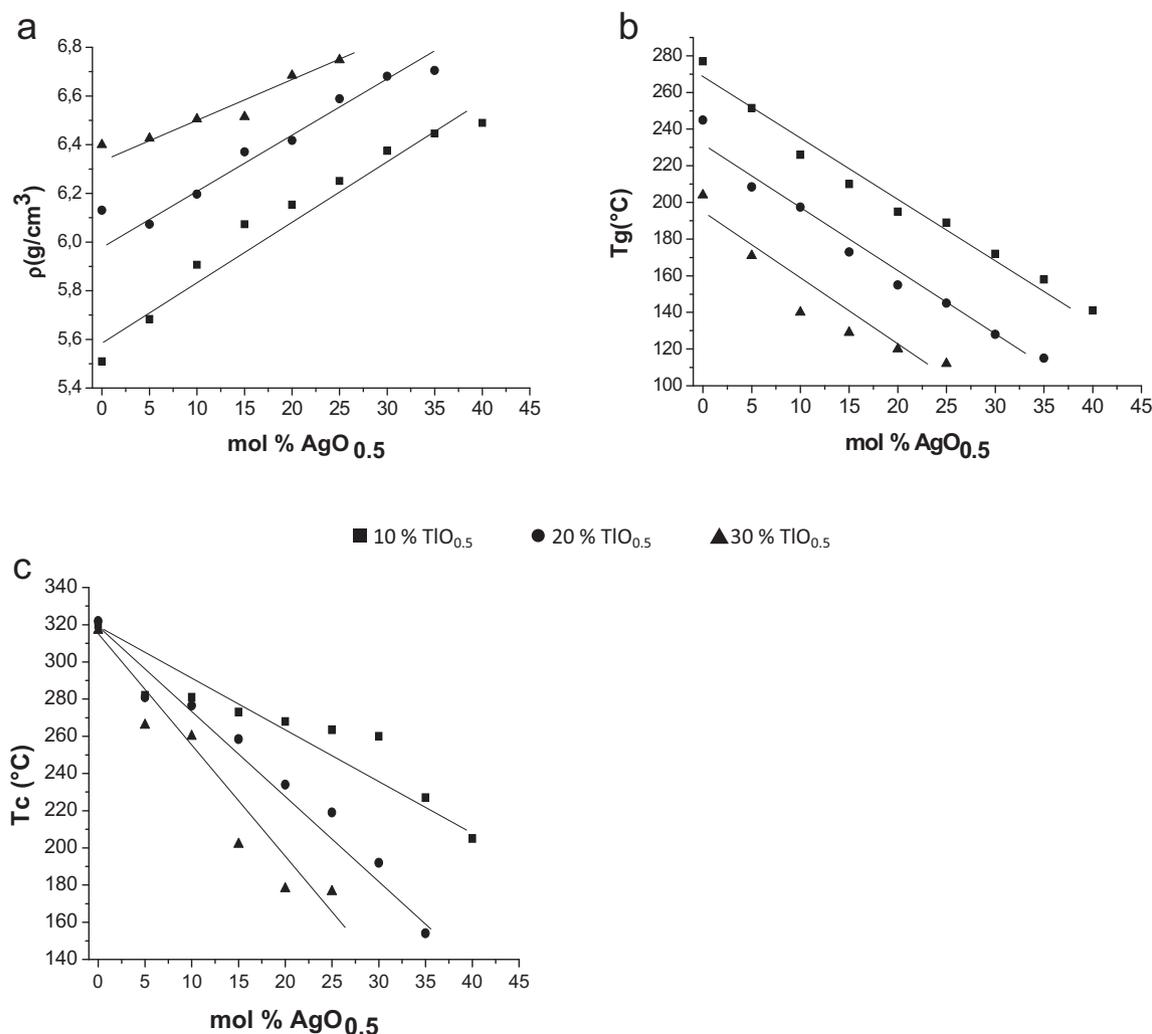


Fig. 2. Evolution with the Ag_2O content of (a) the density ρ , (b, c) the glass transition (T_g) and crystallisation (T_c) temperatures, for some Tl_2O - Ag_2O - TeO_2 glasses.

dependence of the glass density is shown in Table 1 and Fig. 2. The density increases logically with increasing Tl_2O and Ag_2O content, which is in a full correspondence with atomic weight of the adding oxides. As for example the density increases from 5.51 to 7.2 for 90TeO_2 - $10\text{TlO}_{0.5}$ and $55\text{TlO}_{0.5}$ - $5\text{AgO}_{0.5}$ - 40TeO_2 glasses, respectively. One observes for all the glassy samples a continuous decrease of T_g and T_c with increasing concentration of both Ag_2O and Tl_2O . These results suggest that the addition of a modifier oxide like Ag_2O leads to a progressive change from a highly polymerized network in which the TeO_4 disphenoids are linked together via bridging-oxygen corners to a more depolymerised network involving mainly TeO_3 units with bridging and non-bridging oxygen atoms.

The evolution of $(T_c - T_g)$, which in fact characterizes the thermal stability of glasses (see values in Table 1), is more complex. It first slightly increases and then weakly decreases for higher Ag_2O content. So, the addition of Ag_2O to TeO_2 - Tl_2O glasses leads to decrease their thermal stability (parameter we have to take into account to elaborate glass pellets and to process to Raman analysis), and that all the more as they are richer in Tl_2O .

3.3. Vibrational spectra

The Raman spectra of the glasses within the ternary $z\text{TlO}_{0.5}$ - $y\text{AgO}_{0.5}$ - $x\text{TeO}_2$ system were studied in our work along the two

following lines (AB) and (CD) of the phase diagram varying firstly z and keeping $y = 5$ (AB) and then varying y and keeping $x/z = 2.33$ (CD) (see Fig. 1). As the spectra for $y = 5, 10, 15, 20, 25$ and 30 are quite similar, only these recorded for $y = 5$ are presented in this paper. The first line (AB) evidences the Tl_2O influence and the second one (CD) points out the Ag_2O effect on the binary TeO_2 - Tl_2O system. The Raman spectra evolutions are given, respectively, in Figs. 3 and 4. The spectra of the pure TeO_2 glass, crystalline structures γ - TeO_2 , Tl_2TeO_3 and Ag_2TeO_3 are added for better understanding.

Each spectrum has been divided by its average value, to correct intensity fluctuations which might originate from defocusing. Possible laser intensity fluctuations are also corrected by this way. Using the FOCUS program [26], Raman spectra have been decomposed using Gaussian functions for all oscillators, except for boson peak which has been simulated by using a lognormal function.

During the decomposition procedure, the idea of a phase separation within a M_2O - TeO_2 glassy system, preliminary illustrated in [6], was kept in mind (see Section 4). Therefore, it was implied that the Raman spectra of the glasses under study could be presented as a superposition of two spectra: that of tellurium dioxide, and that of M-orthotellurite. Consequently, the glass decomposition had to be based on the initial set of the Gaussian oscillator parameters estimated from the spectra of pure TeO_2 and of pure Tl_2TeO_3 (or Ag_2TeO_3).

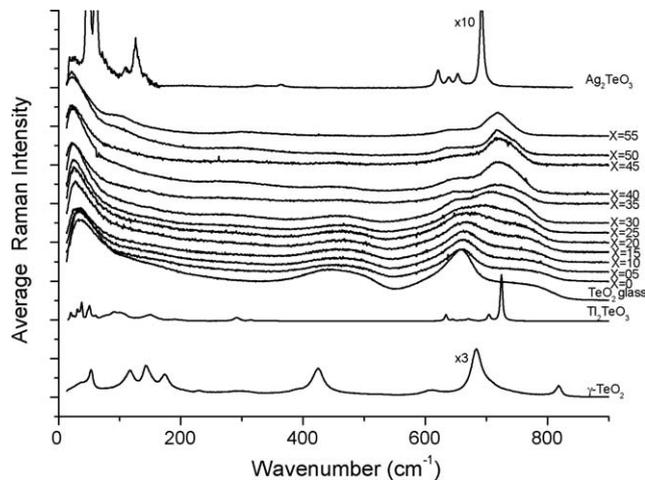


Fig. 3. Raman spectra of the $x\text{TlO}_{0.5}-5\text{AgO}_{0.5}-(95-x)\text{TeO}_2$ glasses, comparing to the spectra of γTeO_2 , Tl_2TeO_3 and Ag_2TeO_3 crystalline lattices. Magnification of Raman spectra ($10\times$, $3\times$).

Since the Raman spectra evolutions offering the information about the structural evolution of our glasses were located above 400 cm^{-1} , our attention was mainly focussed at this part of the spectra, and the relevant spectra decomposition results are shown in Figs. 5–7.

In analyzing these results jointly with the relevant data from the earlier works [6], one can conclude that, theoretically, the spectrum of the TeO_2 – Tl_2O glassy system (Fig. 6 for $y = 0$) in the 400 – 800 cm^{-1} interval should contain ten oscillators, six of which belonging to TeO_2 spectrum, and four to Tl_2TeO_3 spectrum. However, three oscillators belonging to the different spectra have practically the same frequencies. The three pairs which can be found are: one (X) near 620 cm^{-1} , another (Y) near 660 cm^{-1} and the third (Z) near 725 cm^{-1} . So, to augment the objectivity of our decomposition, the number of the independent oscillators above 550 cm^{-1} was found necessary (and possible) to be reduced to five. The three of them, Y , Z and X placed in intervals $660 \pm 5\text{ cm}^{-1}$, $725 \pm 5\text{ cm}^{-1}$ and $620 \pm 5\text{ cm}^{-1}$ were mainly related to the strongest lines dominating the spectra of TeO_2 and Tl_2TeO_3 (or Ag_2TeO_3), respectively. One more oscillator L ($780 \pm 5\text{ cm}^{-1}$) was found necessary to reproduce a wide high-frequency shoulder (700 –

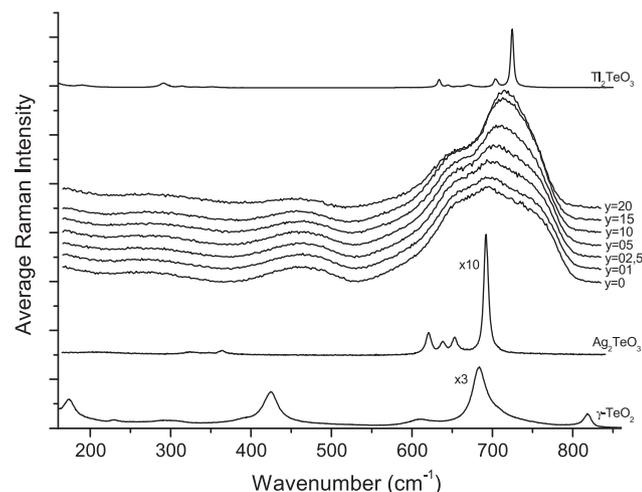


Fig. 4. Raman spectra of the $x\text{TlO}_{0.5}-y\text{AgO}_{0.5}-(100-x-y)\text{TeO}_2$ glasses (with $((100-x-y)/x) = 2.33$), comparing to the spectra of γTeO_2 , Tl_2TeO_3 and Ag_2TeO_3 crystalline lattices. Magnification of Raman spectra ($10\times$, $3\times$).

800 cm^{-1}) of TeO_2 . One weak oscillator K was posed in intervals $706 \pm 5\text{ cm}^{-1}$ to reproduce the highest frequency part of the line dominating the Tl_2TeO_3 glass spectrum.

So, the seven oscillators model's was accepted implying that the two oscillators describing the band in the 400 – 500 range, as well as the oscillator near 780 cm^{-1} are defined indications of the presence of TeO_2 glass, whereas the interpretations of the oscillators near 620 , 660 and 725 cm^{-1} are dual.

According to ideas exposed in Ref. [6], Tl_2O is a strong modifier for TeO_2 glass. Its increasing content in the ternary $(100-x-y)\text{TeO}_2-x\text{TlO}_{0.5}-y\text{AgO}_{0.5}$ system would stimulate quite apparent effect, namely, the formation of the $[\text{TeO}_3^{2-}]$ tellurite ortho-anions, and consequently, the progressive transformation of the initial TeO_2 framework into the island-type Tl_2TeO_3 ortho-tellurite structure. Indeed, the Raman spectra of this system (Figs. 3 and 7) reflect such a transformation (line AB), in manifesting the following changes for the vibrational bands lying above 400 cm^{-1} .

(i) In the 400 – 500 cm^{-1} frequency range (totally related to the TeO_2 vibrations):

- The intensity of oscillators M and N (labelled below I_M and I_N) progressively drops and vanishes at $x = 45$, while oscillator's frequency is kept.

The progressive decay and final vanishing of the M and N oscillators unequivocally indicates the disappearance of the TeO_2 framework (more correctly, its transformation into the Tl_2TeO_3 ortho-tellurite phase).

(ii) In the 550 – 800 cm^{-1} frequency range:

- Intensity I_X has a maximum value at about $x = 0$, and decreases similar to that of I_M and I_N .
- The intensity I_Y is equal to that of I_Z for about $x = 25$ and then decreases while the intensity of the oscillator Z increases.

In fact, the above-mentioned evolution of the spectra displays some sort of a competition between the Tl_2TeO_3 and TeO_2 phases, which is clearly seen in the decreasing intensity of the band specific of glassy TeO_2 and the increasing intensities of those specific of glassy Tl_2TeO_3 .

We now turn our attention on the spectra of the $x\text{TlO}_{0.5}-y\text{AgO}_{0.5}-(100-x-y)\text{TeO}_2$ glassy system (line CD see Fig. 1). Figs. 4 and 6 show that with increasing content of Ag_2O in $x\text{TlO}_{0.5}-y\text{AgO}_{0.5}-(100-x-y)\text{TeO}_2$ glassy system (with $(100-x-y)/x = 2.33$) the same effects are observable in the spectra. Actually, being decomposed along the above-described seven-oscillators schema (the intensity of those oscillators are named I_M , I_N , I_X , I_Y , I_K , I_Z and I_L , respectively) those spectra show the following peculiarities:

- The ratio $(I_X + I_Y/I_K + I_Z + I_L)$ decreases, thus manifesting the TeO_2 content decrease with respect to the increase of Tl_2TeO_3 content.
- In line with this, the decrease of the ratio $(I_M + I_N)/(I_X + I_Y + I_Z + I_L + I_K)$ evidences the progressive disappearance of Te-O-Te bridges associated with the $[\text{TeO}_3]^{2-}$ ortho-anions formation.

4. Discussion

The Raman spectra of binary TeO_2 – Tl_2O glasses are known from the pioneering works by Sekiya et al. [11]. Since then, they were reinvestigated jointly with those of binary TeO_2 – Ag_2O glassy system [1,10,20–22], and recently [6], they were reconsidered following the approach of the phase separation effects expected by tellurite glasses with strong modifiers.

Consequently, the band positions in those spectra of pure TeO_2 , Tl_2TeO_3 and Ag_2TeO_3 glasses are well documented. The spectra of

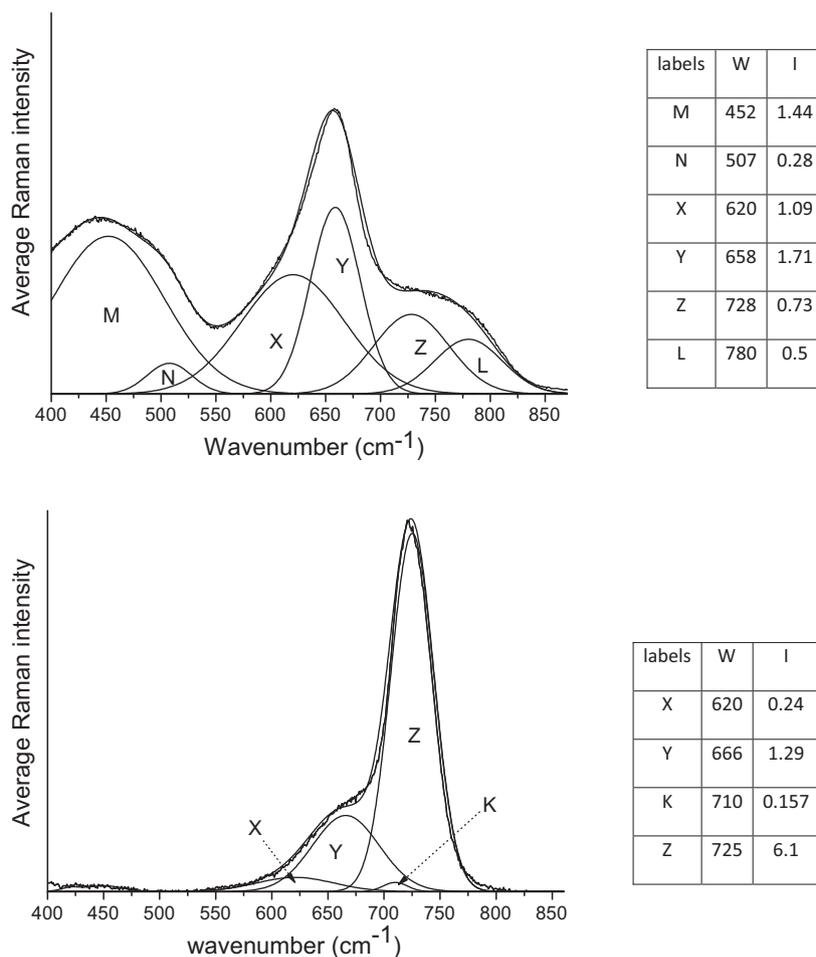


Fig. 5. Decomposition of baseline-corrected Raman spectra of TeO_2 and Tl_2TeO_3 glass.

the two latter glasses perfectly envelope the spectra of the corresponding ortho-tellurite crystal lattices [6], thus indicating that the anionic systems of those glasses consist of regular pyramid-like $[\text{TeO}_3]^{2-}$ ortho-anions whose geometries practically coincide with their crystalline homologues. The strongest and highest-frequency Raman-active bands in the spectra of Tl_2TeO_3 and Ag_2TeO_3 glasses are located around 692 and 725 cm^{-1} , respectively, and correspond undoubtedly to the A_1 stretching modes of the $[\text{TeO}_3]^{2-}$ species (in a C_{3v} symmetry nomenclature), whereas the groups of weak bands below 700 cm^{-1} correspond to the E component of such modes [6].

It must be noted that, according to the structural studies of crystalline Ag_2TeO_3 [23] and Tl_2TeO_3 [12], the Te–O bond lengths are practically equivalent in both crystals (1.872 ± 0.005 Å). However, this is in conflict with the fact that the A_1 stretching mode position in the spectrum of crystalline Ag_2TeO_3 is markedly lower than in the spectrum of Tl_2TeO_3 , which implies that the Te–O bonds in the former lattice must be longer than that in the latter.

Our further speculations concerning the structural interpretation of the Raman spectra evolution in Figs. 3 and 4 are based on the suggestion of the phase separation effect expected in the glasses under study. To understand the reasoning behind this suggestion, the two following points must be taken into account:

(i) Tellurium dioxide TeO_2 in its fundamental state (paratellurite) is a molecular crystal [6], and therefore melted tellurium dioxide would consist in TeO_2 molecular-like species.

(ii) In complex oxides $n\text{TeO}_2 + \sum_j k_j \text{M}_j\text{O}$ under our study, the M^+-O bonds are much weaker than Te–O ones.

For simplicity, let us consider a two-component system, $n\text{TeO}_2 + k\text{M}_2\text{O}$ ($n > k$). After melting, according to points (i) and (ii), our liquid system would contain n neutral TeO_2 molecules coming from the former component, to which M^+ cations ($2k$ pieces) and O^{2-} anions (k pieces) would be added from the latter component. A reaction minimizing the electron energy of the system would rearrange such a mixture into a tellurite compound by forming a third bond around each Te, $\text{TeO}_2 + \text{O}^{2-} = [\text{TeO}_3]^{2-}$ (thus it can be said that the M_2O modifier plays, first of all, the role of a supplier of the oxygen anions necessary for just mentioned reaction).

As a result, k ortho-anions $[\text{TeO}_3]^{2-}$ would appear, and the system chemical composition would become $(n-k)\text{TeO}_2 + k[-\text{TeO}_3]^{2-} + 2k\text{M}^+$. The further minimization of its energy is driven by the strongest electrostatic (monopole–monopole) interactions between the $[\text{TeO}_3]^{2-}$ ortho-anions and M^+ cations, on the one hand, and dipole–dipole interaction between TeO_2 species, on the other hand. For this, the $[\text{TeO}_3]^{2-}-\text{M}^+$ and $\text{TeO}_2-\text{TeO}_2$ distances should be diminished as possible, thus leading to the formation of micro-domains of pure M_2TeO_3 and $\alpha\text{-TeO}_2$, i.e., to a phase separation phenomenon.

Therefore, it can be thought that, the effect of phase separation should be inherent in all the glasses having monovalent cations M^+ . Consequently, their chemical compositions can be always given by the expression $(n-k)\text{TeO}_2 + k\text{M}_2\text{TeO}_3$ and (for $n > k > 0$) the structural evolution of such a glass with augmenting k would just correspond to the M_2TeO_3 content increase and to the TeO_2 content decrease, respectively.

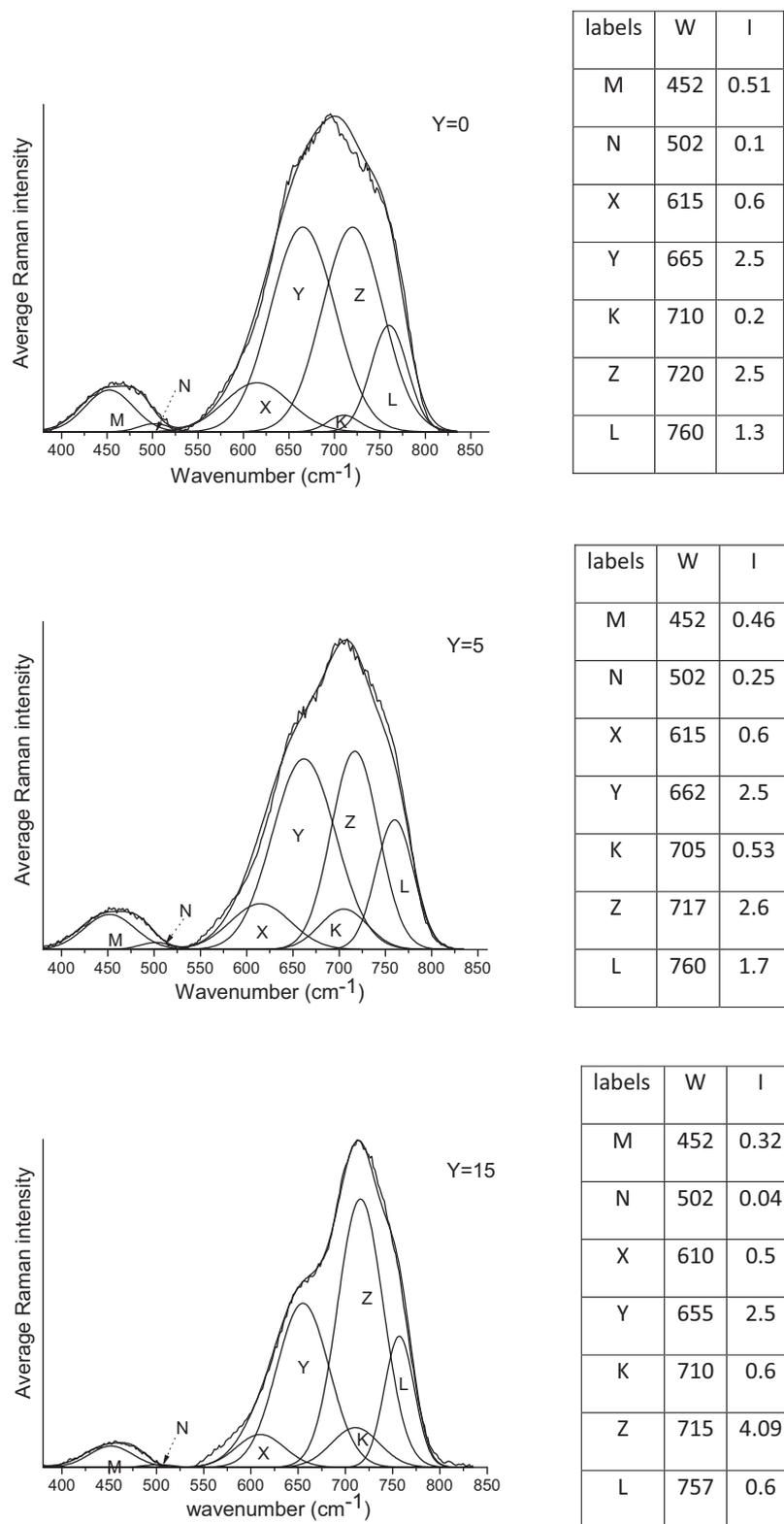


Fig. 6. Decomposition of baseline-corrected Raman spectra of some $x\text{TiO}_{0.5-y}\text{AgO}_{0.5-(100-x-y)}\text{TeO}_2$ glasses (with $((100-x-y)/x) = 2.33$) (using the Gaussian-like oscillators, K–N, X–Z). Line (AB). The insets show the oscillators characteristics: frequencies expressed in wavenumbers w , and normalized intensity I .

The above ideas have been already applied to the $n\text{TeO}_2-k\text{Ti}_2\text{O}$ glassy system [6], and allowed explicating the following facts: (i) at increasing k , no complex tellurite anions other than $[\text{TeO}_3]^{2-}$ (i.e., $[\text{Te}_3\text{O}_7]^{2-}$, $[\text{Te}_2\text{O}_5]^{2-}$, $[\text{Te}_3\text{O}_7]^{2-}$, $[\text{Te}_4\text{O}_9]^{2-}$, etc.) were evidenced; (ii) the shapes of the Raman spectra of the relevant glasses (see e.g. Fig. 6, $y = 0$) could be always reproduced as a superposition of the spectra of

the two individual phases mentioned above, including a strong “line-phantom” which appeared near 700 cm^{-1} when $n \sim 4k$. The existence of that line is an important experimental argument in favour of the phase separation in $n\text{TeO}_2-k\text{Ti}_2\text{O}$ glassy system.

Actually, as an alternative to the process of the separation into pure TeO_2 and Ti_2TeO_3 phases, the formation of a glass containing

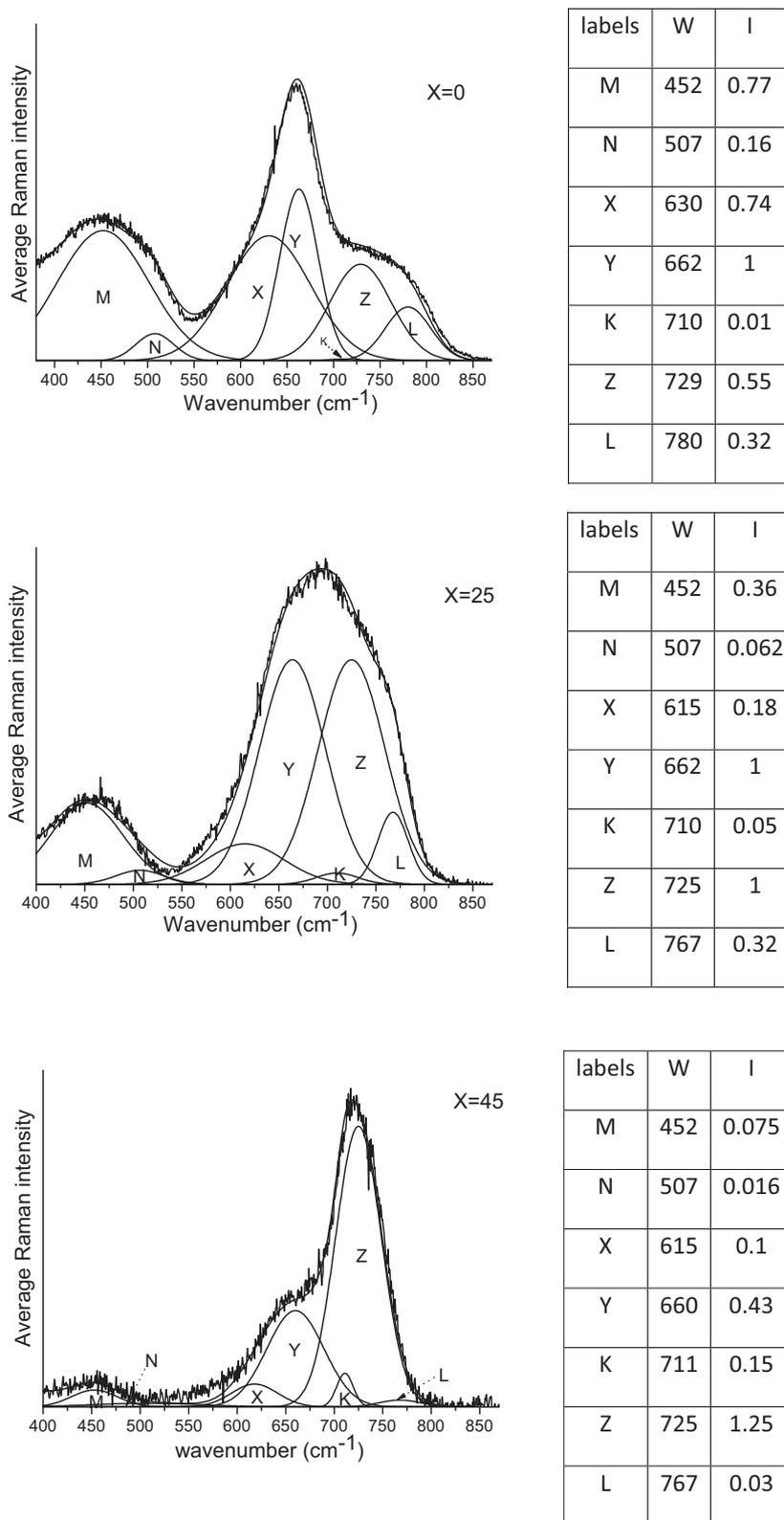


Fig. 7. Decomposition of baseline-corrected Raman spectra of some $x\text{TlO}_{0.5}-5\text{AgO}_{0.5}-(95-x)\text{TeO}_2$ glasses (using the Gaussian-like oscillators, $K-N, X-Z$). Line (CD). The insets show the oscillators characteristics: frequencies expressed in wavenumbers w , and normalized intensity I .

chain-like $[\text{Te}_n\text{O}_{2n+1}]^{2-}$ ($n = 2-4$) anions could be expected for the $n\text{TeO}_2-k\text{Tl}_2\text{O}$ system with increasing k . Consequently, the appearance of a new strong peak near 700 cm^{-1} could be interpreted as indicative of any of such anions. However, the Raman spectra of those anions are documented in Refs. [5,9], and they cannot be related to that band. At the same time, that peak was found readily

reproducible when describing the spectrum just as a superposition of the spectra of TeO_2 and Tl_2TeO_3 glasses [6], i.e., without supposed any oscillator near 700 cm^{-1} .

The data on the composition dependence of the Raman spectra of the binary $\text{TeO}_2-\text{Ag}_2\text{O}$ glasses [20] manifest apparently the same peculiarities as the spectra of binary $\text{TeO}_2-\text{Tl}_2\text{O}$ system. Therefore,

all the logic of the above made consideration stays valid for the $\text{TeO}_2\text{-Ag}_2\text{O}$ glasses.

The main question in our present study concerns the properties of ternary $x\text{TlO}_{0.5} + y\text{AgO}_{0.5} + (100-x-y)\text{TeO}_2$ glassy system. Fig. 6 is concerned with the compositions with constant $(100-x-y)/x = 2.33$, and y varying between 0 and 15. For $y = 0, x = 30$, the band $600\text{--}700\text{ cm}^{-1}$ in Fig. 6 has quite symmetric shape. The peak near 700 cm^{-1} is well seen there, and seems to be even more pronounced than in previous work on $\text{TeO}_2\text{-Ag}_2\text{O}$ binary glassy system [20–22]. At slightly increasing y , i.e. when the second modifier is added, the peak displaces at higher frequencies and disappears for $y = 5$, whereas the left-hand side of the band fall down, and the right-hand side grows up, thus making the band more and more asymmetric. For $y = 15$, the spectrum is dominated by a strong line centred near 715 cm^{-1} . At the same time, a marked decreasing of the Raman scattering intensity in the $400\text{--}500\text{ cm}^{-1}$ and $600\text{--}680\text{ cm}^{-1}$ interval is observed.

To explain such behaviour of the spectra, it should be taken into account that Ag_2O is an oxygen supplier just as Tl_2O , and that the Ag^+ and Tl^+ cations bear the same charge. Then there is a good reason to suppose that: (i) the chemical evolution of our ternary glasses would follow the same aforementioned energetic principles; (ii) the glasses would consist of two phases only: one of pure TeO_2 , and one of pure ortho-tellurite with the statistically mixed Ag-Tl cationic system, so that for $y = 15$ the glass composition would be $49.2\text{TeO}_2 + 25.4(\text{Ag}_{0.37}\text{Tl}_{0.63})_2\text{TeO}_3$.

To argue for the just mentioned points (i) and (ii), a decomposition of the wide band lying over the $550\text{--}800\text{ cm}^{-1}$ range was made for fixed $(100-x-y)/x = 2.33$, and $y = 0, 5, 15$.

The spectrum for $y = 0$ in Fig. 6 corresponds to the glass in which the molar concentrations of TeO_2 and Tl_2O are in the ratio 14:3, which means that the relative amounts of the TeO_2 and Tl_2TeO_3 phases are in the ratio 11:3. The decomposition results presented in Fig. 6 show that no oscillators other than those belonging to pure TeO_2 and Tl_2TeO_3 are necessary to reproduce the “new” peak near 700 cm^{-1} simultaneously with all other peculiarities of the band’s shape.

We wish to note that in the spectrum in Fig. 6 for $y = 0$ obtained for $\text{TeO}_2/\text{Tl}_2\text{TeO}_3$ content ratio equal to $7/2$, the oscillator Y (658 cm^{-1}), mainly representing the Te-O stretching vibrations of the TeO_2 quasi-molecules in TeO_2 phase, has the same intensity as the oscillator Z (725 cm^{-1}) mainly representing the Te-O stretching vibrations of the $[\text{TeO}_3]^{2-}$ ortho-anions in the Tl_2TeO_3 phase. This observation allowed as thinking that the absolute intensities of the X and Z oscillators are in inverse ratio, i.e. close to $2/7$.

When $y = 5$, the band in general becomes narrower and the peak is more displayed and distinguished. Again, the shape of this band is easily reproducible using the same five oscillators in which, however, the oscillator positions sensible to the increasing number of the $[\text{TeO}_3]^{2-}$ ortho-anions shift to lower frequencies. The spectrum for $y = 15$ also manifests the same reproducibility within the five-oscillator model, and the same oscillators shifts to the left. So the behaviours of the Raman spectra of the $x\text{TlO}_{0.5} + y\text{AgO}_{0.5} + (100-x-y)\text{TeO}_2$ system with the increasing y/x ratio manifest a continuous displacement of the oscillator initially ($y = 0$) placed in the position inherent in the Tl_2TeO_3 Raman spectrum to the position inherent to the Ag_2TeO_3 spectrum. In particular, for $y = 15$ (i.e., for $y/x = 2/3$), the oscillator, initially ($y = 0$) characteristic for pure Tl_2TeO_3 , is just displaced into the position intermediate between those characteristic for Tl_2TeO_3 and for Ag_2TeO_3 . We wish to underline that no other oscillator specifying the $[\text{TeO}_3]^{2-}$ ortho-anion is necessary. Such an evidence leads to conclude that the ternary glasses under consideration always comprise two phases: TeO_2 and $(\text{Ag}/\text{Tl})_2\text{TeO}_3$.

5. Conclusion

Addition of silver oxide to thallium tellurite glasses has allowed the formation of a large glassy system but has not improved the thermal stability of the ternary glasses thus obtained. The Raman spectroscopic investigations of these glasses have confirmed the existence of a phase separation effect previously evidenced in thallium tellurite glasses: the shapes of the Raman spectra were found to be always reproducible as a superposition of the spectra of pure TeO_2 phase and of pure ortho-tellurite M_2TeO_3 ($\text{M} = \text{Ag}, \text{Tl}$) phase. Thus the present study confirms that tellurite glasses doped with weak cations (i.e. low valence) possess a strong tendency to immiscibility behaviour due to the separation in the melts into pure TeO_2 phase and that of M_2TeO_3 formulation. The increasing content of weak Ag^+ cation stimulates the effect of the glassy network depolymerisation, which evidently cannot augment its thermal stability.

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