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Synthesis and characterization of new amorphous and crystalline phases in Bi_2O_3-Ta_2O_5-TeO_2 system

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Abstract
A glass-forming domain is found and studied within Bi_2O_3– Ta_2O_5–TeO_2 system. The glasses obtained in the system Ta_2O_5-TeO_2 was investigated by DSC, Raman and Infrared spectroscopy. The influence of a gradual addition of the modifier oxides Ta_2O_5 on the coordination geometry of tellurium atoms has been elucidated based Infrared and Raman studies and showed the transition of TeO_4, TeO_{3+1} and TeO_3 units with increasing Ta_2O_5 content. The density of glasses has been measured. The investigation in the TeO_2- Ta_2O_5 system using XRD reveals new phases.

Keywords*: X Ray Diffraction -DSC - IR- Glass transition - Tellurite glasses*

1. Introduction
The enhanced nonlinear optical materials have attracted much interest with novel applications in optoelectronics, optical switchers and limiters, as well as in optical computers, optical memory, and nonlinear spectroscopy. Tellurite glasses, due to their wide infrared window, excellent chemical durability and stability, ultra-fast nonlinear optical response and excellent third-order optical nonlinearity, have noticeable advantages in comparison with other conventional glasses, which makethe tellurite glasses especially attractive in a variety of practical applications. Recently, the interest on tellurite glasses is focused on their high refractive index. Tellurite glasses in the systems such as TeO_2–Nb_2O_5, TeO_2–Nb_2O_5–ZnO, TeO_2–Bi_2O_3–ZnO, TeO_2–TiO_2–BaO, TeO_2–TiO_2–Bi_2O_3 and TeO_2–TiO_2–Nb_2O_5 have been demonstrated to have excellent nonlinear optical performances [1–6]. Therefore, abundant researches are focused on producing new tellurite glasses of improved optical properties.
The present paper reports a preliminary investigation of new tellurite glasses and crystalline phases in Bi_2O_3–Ta_2O_5–TeO_2 system. Elaboration process, thermal properties infrared (IR) and Ramann studies in comparison to analogous crystalline phases will be described successively.

2. Experimental
The amorphous and crystalline samples were prepared using high purity commercial materials Bi_2O_3, TeO_2 Ta_2O_5 of analytical grade (Aldrich 99.9%). The batches of suitable proportions of starting products were mixed in an agate mortar and then heated in air at 800°C (20 min) for vitreous phases and at 600°C-800°C (48h) for crystalline phases. All of them are quenched to room temperature and identified by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (Cu-K-alpha radiation). Tg (glass temperature) and Tc (crystallization temperature) were determined using Differential Scanning Calorimetry (DSC) Netsch 2000 PC

type from powder samples glasses for about 8mg in aluminum pans. A heating rate of 10°C/min was used in the 30-650°C range. Infrared absorption measurements between 2000-400 cm^{-1} were made for powder specimens dispersed in a pressed KBr disk. The Raman spectra were recorded in the 80–1000 cm^{-1} range using a Jobin-Yvon spectrometer (64000 model) equipped with an Ar+ laser (514.5 nm exciting line) and a CCD detector in a backscattering geometry. The sample focalization was controlled through a microscope (×100). The diameter of the laser spot focused on the sample was about 1 mm. The spectra were recorded in two scans (during 100 s) at low power (<100 mW) of the excitation line, in order to avoid damage of the glasses. The spectral resolution was about 2.5 cm^{-1} at the exciting line. The densities of samples were measured according to the Archimedes's principle using diethylorthophtalat as solvent.

3. Results and discussion

A wide range glass system based on the Bi_2O_3–Ta_2O_5-TeO_2 system was prepared at 800°C after a series of composition. the vitroeus was determinated by X-ray diffraction . This temperature have been chosen to have a homogenous reagent in one hand and to avoid volatization of TeO_2 at high temperature ($T_{TeO2Melting}$=732°C) on the other hand (Figure 1). The color of the glass changes slightly from dark yellow to yellow with increasing Ta_2O_5 and Bi_2O_3 concentration.

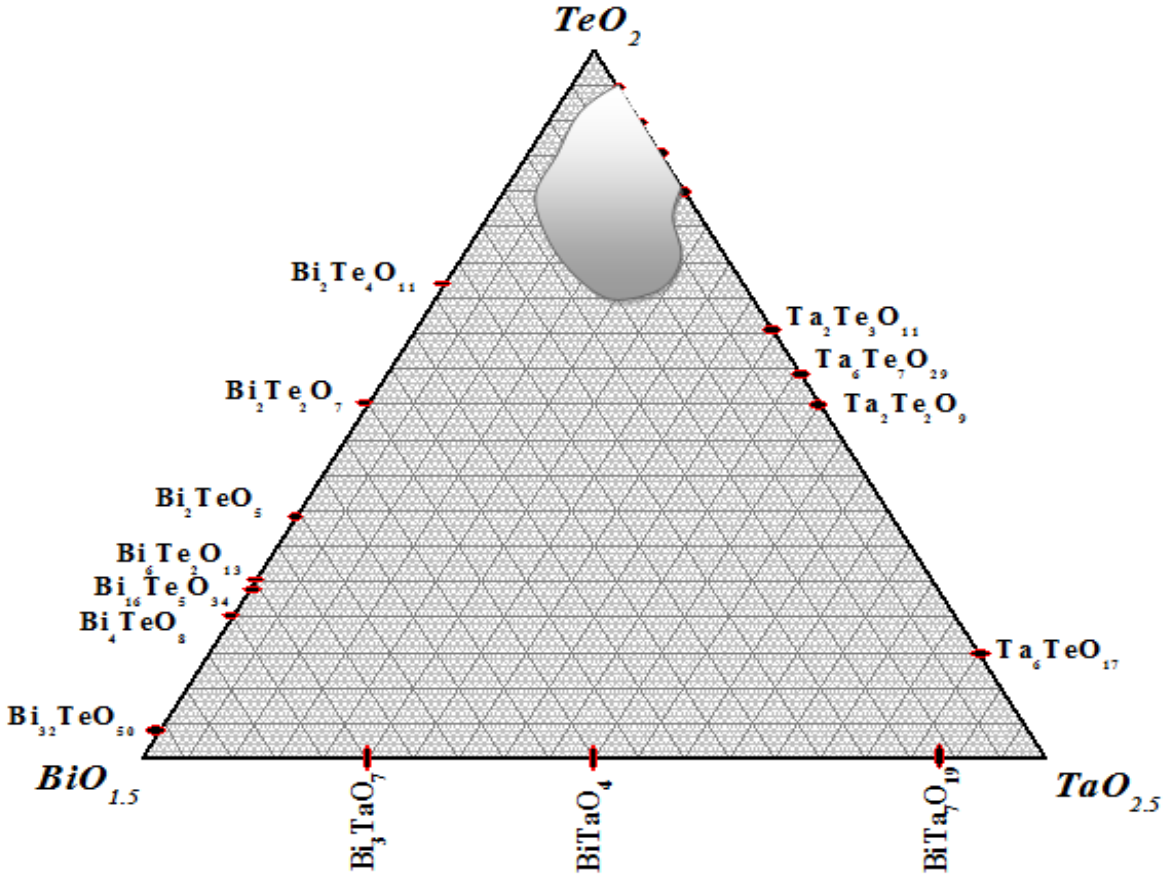

Figure 1: Vitreous domain diagram for the Bi_2O_3-TeO_2-Ta_2O_5 system

3.1. Differential scanning calorimetry(DSC)

Series of glasses composition are listed in (Table 1). An addition of $TaO_{2.5}$ (up to 0.5 mol%) would result in the increase of glass stability (as indicated by Tc–Tg). This is presumably due to the participation of Ta^{5+}in the glass network. The values of Tg, Tc_1, Tc_2 and Tc_3 are presented (Figure 2) and (Table 1).

Table 1: Characteristics (Tg, Tc) and difference (Tc_1 −Tg) of some glasses in the Ta_2O_5–TeO_2–Bi_2O_3 system.

%TeO_2	% $TaO_{2.5}$	Tg (°C)	Tc_1 (°C)	Tc_2 (°C)	Tc_3 (°C)	Tc_1-Tg (°C)
95	5	378	490	522	595	112
90	10	380	412	518	572	38
85	15	382	461	516	576	79

The curves (DSC) exhibit an endothermic effect due to glass transition (Tg), and shows that tree exothermic phenomenon occurred at (Tc_1), (Tc_2) and (Tc_3), du to the formation of different cristalline phases. The appearance of single peak (all glasses) due the glass transition temperature Tg indicates the homogeneity of the glasses prepared. With increasing of Ta_2O_5 content in the glass matrix, the Tg increases and the difference (Tc-Tg) (about 79-112°C) implies a thermal stability of glasses (Figure 2).
In a study of alkali tellurite glasses, Pye et al [7] showed that the temperature of the glass transition decreases with increasing amount of Li, Na or K compound. The dependence of Ta_2O_5 content shows a different tendency especially of glass transition compared with the alkali tellurite glasses. The alkali atoms easily move in the glass structure. The light change of the temperature of crystallization of a vitreous composition to another is due to the kinetic phenomenon. Based on XRD and DSC analysis for glassy samples 5-20 mol % $TaO_{2.5}$ (Figure 3a). The first peak of crystallization corresponds to the γTeO_2, αTeO_2 and $Ta_2Te_3O_{11}$ at 500°C. This phenomenon which we observed, i.e the crystallization of γ TeO_2 variety is also obtained in the many systems as TeO_2-WO_3 [10], Nb_2O_5-TeO_2 [8,11], TeO_2-ZnO [12], TeO_2-SrO [13] and Sb_2O_3-TeO_2 [14]. In second crystallization at 550°C belongs to reinforcing $Ta_2Te_3O_{11}$ and αTeO_2 phases. The last peak (650°C) with weak intensity is attributed to totally transformation γTeO_2 metastable polymorph into the stable αTeO_2 and $Ta_2Te_3O_{11}$.

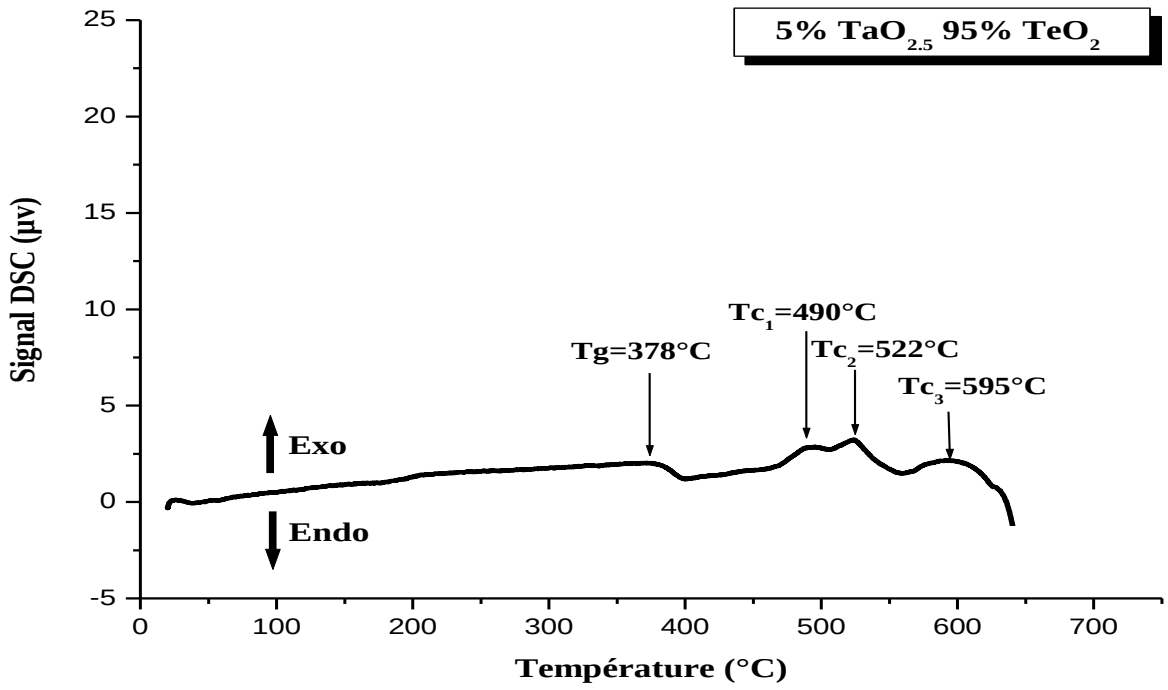

Figure 2 : DSC curves of glassy samples obtained in $xTaO_{2.5}$, $(1-x)TeO_2$ pseudo- binary ($0.05 \leq x \leq 0.15$)

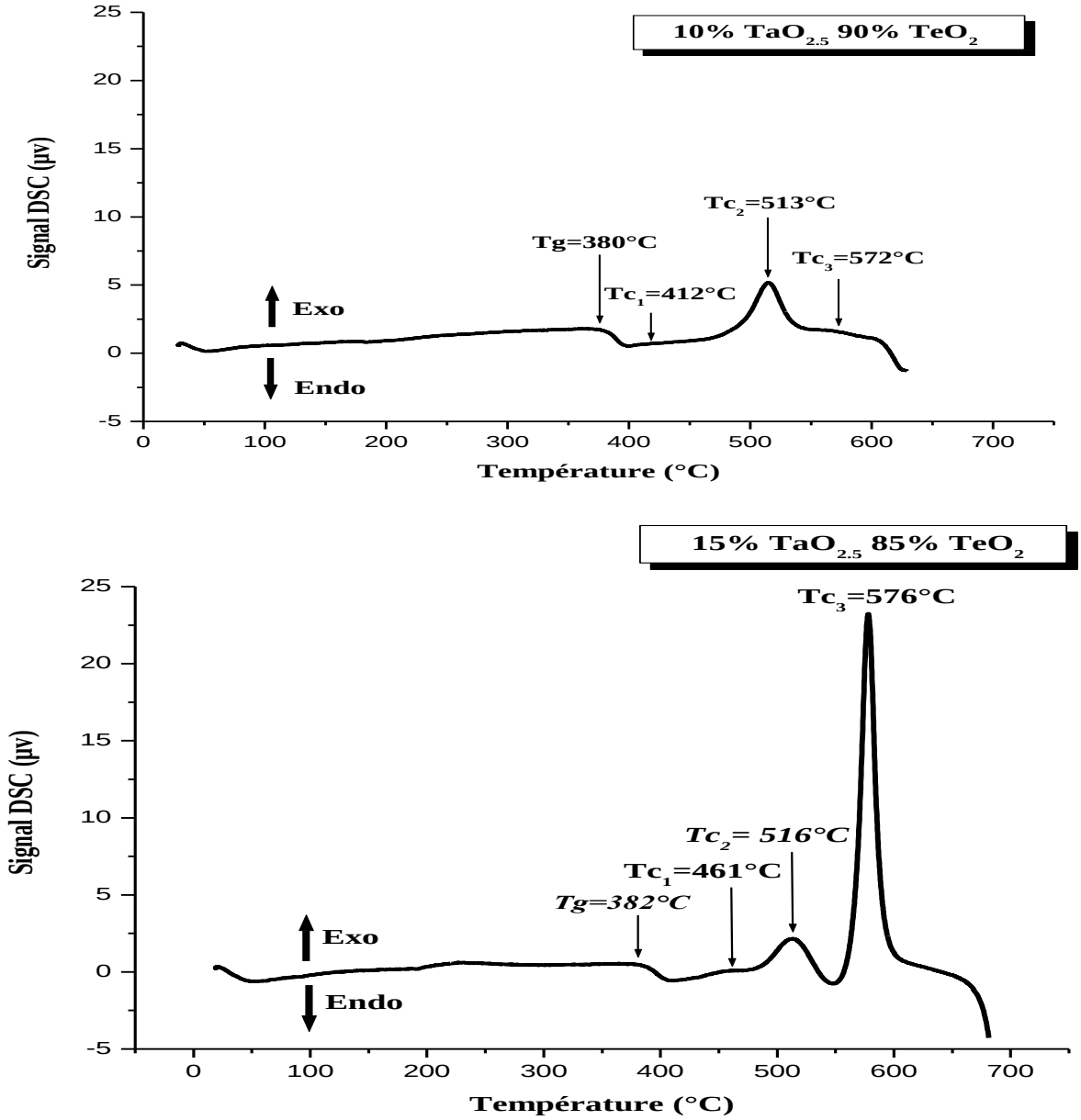

Figure 2bis : DSC curves of glassy samples obtained in $xTaO_{2.5}$, $(1-x)TeO_2$ pseudo- binary ($0.05 \leq x \leq 0.15$)

It is important to mention that the thermal analysis curves discussed in paragraph 3-1 of glasses of the pseudo – binary $TeO_2 – TaO_{2.5}$ which have a composition of 15 % mol of $TaO_{2.5}$ exhibit three crystallizations, there X ray diffraction data are plotted in (Figure 3b). The first crystallization occurred within the range of 400°C and 490°C, the X ray diffraction spectra of the crystallized phases gained after a thermal annealing of the composition (85 % TeO_2 , 15% $TaO_{2.5}$) at temperature 500 °C during 24h, shows the existence of a tri-phases mixture: TeO_2 (α), TeO_2 (β) and a new phase called Y.

The second crystallization occurred within the range of 450 °C and 540 °C, a new phase Y showed up after a thermal annealing of the same composition used in the first process of crystallization at a temperature of 500 °C during 24h and disparities of TeO_2 (α) and TeO_2(γ) phases. Finally, the third crystallization which happened within the range of 550 °C and 640 °C and which was thermally annealed at 650°C, exhibits the same behavior as that of second one.

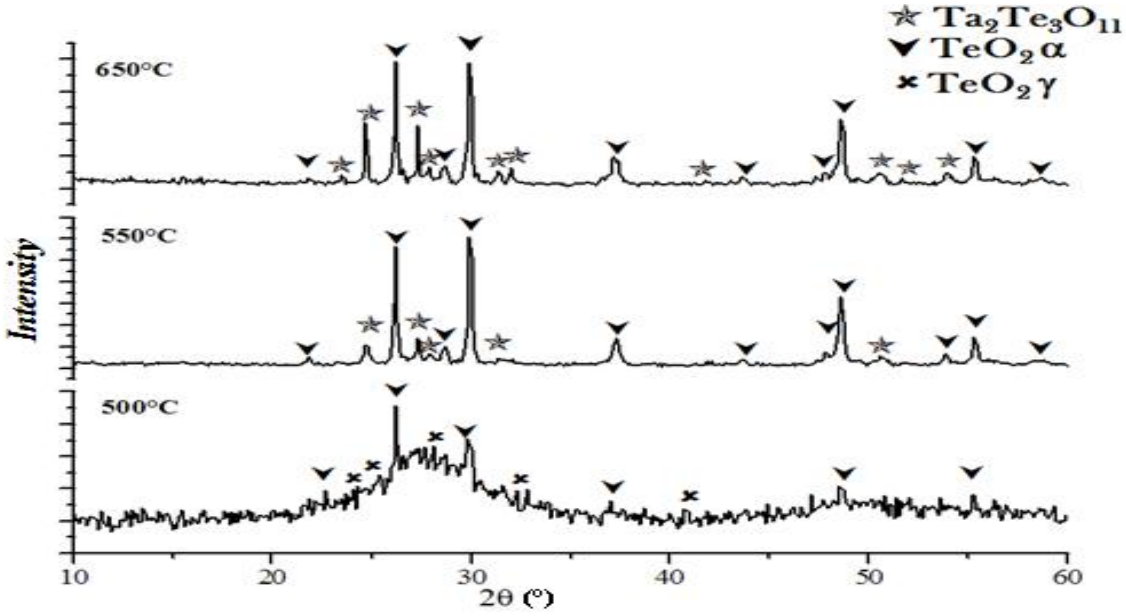

Figure 3a: XRD patterns heat-treated at 500°C, 550°C and 650°C of (90%TeO_2 ,10% $TaO_{2.5}$ mol) in pseudo-binary TeO_2- $TaO_{2.5}$.

The automatic peaks indexation of this new phase Y using program ito [15], provided the following results: M (12) =81 on the basis of monoclinic lattice with a=7.05 Å, b=8.946 Å, c=6.434 Å, β= 100.54° and $V_{lattice}$ = 398.94 $Å^3$ .The reflection conditions are in agreement with space groups C_c and $C_{2/c}$. The indexed powder diffraction pattern is shown in (Table 2). The structural characterization of this phase will be published future article.

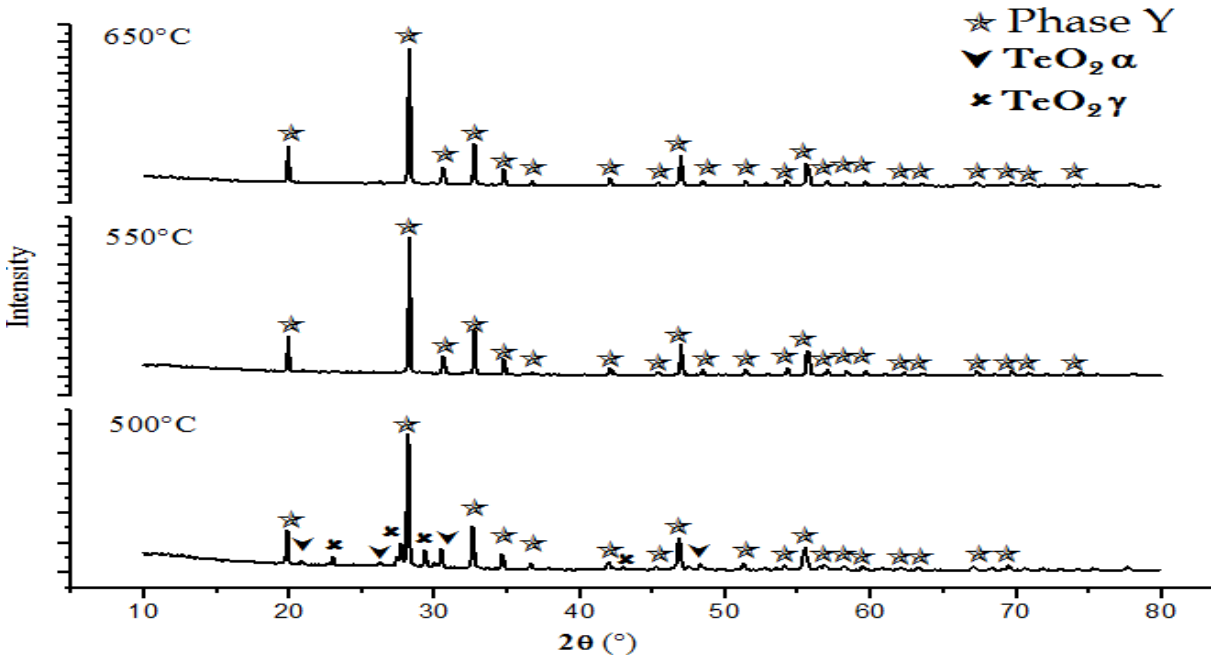

Figure 3b: XRD patterns heat-treated at 500°C, 550°C and 650°C of (85%TeO_2 ,15% $TaO_{2.5}$ mol) in pseudo-binary TeO_2-$TaO_{2.5}$.

Table 2: Indexing of XRD reflections of new phase Y.

h k l	d_{obs} **(Å)**	d_{cal} **(Å)**	I/I_o
1 1 -1	*4.454*	*4.452*	*28*
0 0 2	*3.153*	*3.152*	*100*
1 1 -2	*2.919*	*2.919*	*15*
2 2 0	*2.732*	*2.731*	*33*
1 1 2	*2.575*	*2.576*	*12*
1 3 1	*2.443*	*2.444*	*4*
2 0 2	*2.143*	*2.144*	*6*
3 1 1	*1.996*	*1.997*	*3*
2 2 2	*1.933*	*1.933*	*20*
1 1 3	*1.875*	*1.876*	*5*
2 2 4	*1.714*	*1 .713*	*5*
3 1 -3	*1.688*	*1.688*	*5*
1 5 1	*1.649*	*1.650*	*18*
4 2 0	*1.613*	*1.613*	*5*
0 0 4	*1.579*	*1.579*	*4*
2 0 -4	*1.547*	*1.548*	*4*
0 2 4	*1.489*	*1.489*	*2*
1 1 4	*1.462*	*1.462*	*4*
5 1 -1	*1.390*	*1.390*	*4*
2 0 4	*1.347*	*1.347*	*4*
1 3 4	*1.327*	*1.327*	*3*
5 3 -1	*1.273*	*1.273*	*3*

3.2. Density and molar volume
3.2.1. Experiment procedure
The density of the specimens was measured using Archimeds principle using orthophtalate as the immersion liquid ($d_{orthophtalate}$= 1.11573 at 23.5°C). A glass disc was weighted in air (Wair) and immersed in orthophtalate and reweighted ($W_{orthophtalate}$). The relative density is given by the following relation [16]:

$$d = d_{orthophtalate}\frac{W_{air}}{W_{orthophtalate}}$$

The data from the performed measurements are shown in (Table 3). Moreover, the variation of the density and the molar volume of some composition the pseudo – binary TeO_2-$TaO_{2.5}$ vitreous phases versus the added amount of $TaO_{2.5}$ is illustrated in (Figure 4).
According to the plotted data in (Figure 4), it is obvious that the density of the vitreous phases of the pseudo – binary TeO_2-$TaO_{2.5}$ increases as the rate of $TaO_{2.5}$ increases. However, the molar volume decrease with that same rate of $TaO_{2.5}$ according to increasing Tg. The explanation can provided of this rise of the density lies in the difference between the molar masses of the elements ($M_{TaO2.5} > M_{TeO2}$). Besides, we suppose that the exhibited decrease of molar volume (M) is due to the contraction of the vitreous network, caused by the added $TaO_{2.5}$.

***Table** 3*: Density, and molar volume of some composition the pseudo – binary TeO_2-$TaO_{2.5}$

%mol TeO_2	***% mol $TaO_{2.5}$***	***Density (±0,02)***	***molar volume (M)*** ($Å^3$)
95	*5*	*6.10*	*26.67*
90	*10*	*6.25*	*26.49*
85	*15*	*6.41*	*26.33*
80	*20*	*6.57*	*26.15*

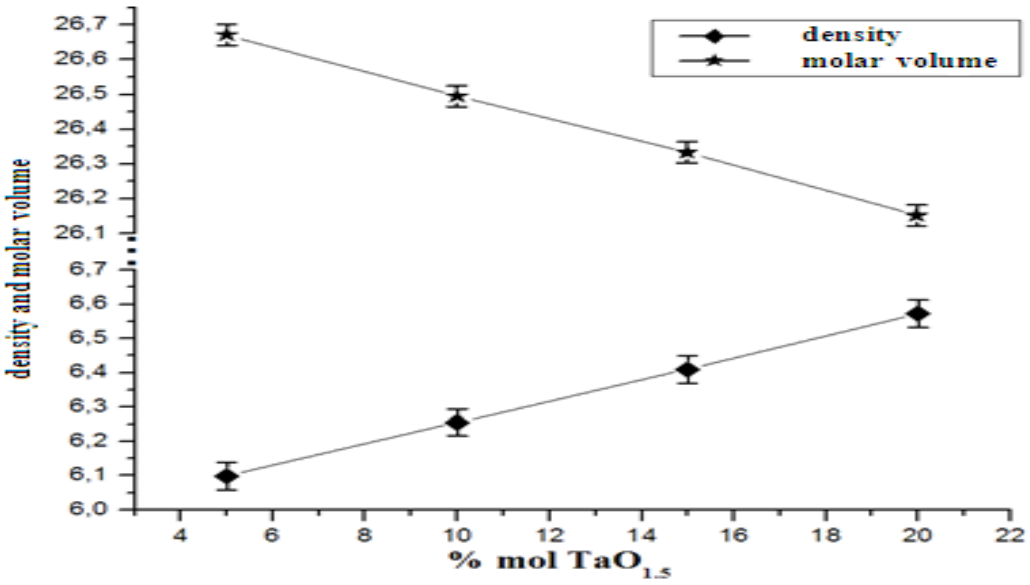

Figure 4: Variation of the density and that of the molar volume of some of the pseudo – binary TeO_2-$TaO_{2.5}$

3.3 Spectroscopy studies

3.3.1 IR study

The bands in the IR spectrum of crystalline TeO_2 are assigned according to C_{2v} point group symmetry in the following manner:

υ (Te-O_{eq}^{s})= 780 cm^{-1}, υ (Te-O_{eq}^{as})=714 cm^{-1}, υ (Te-O_{ax}^{as}) = 675 cm^{-1} et υ (Te-O_{ax}^{s}) = 635 cm^{-1}.

In the pure TeO_2 glass the υ^s band at 635cm^{-1} increases markedly instated of v^{as} TeOax = 675cm^{-1} and becomes a determining one. The rise of v_{ax}s intensity is the result of decrease in the symmetry of the polyhedra in the glass network [17−19].

IR spectra of tellurite built up by TeO_3 polyhedra with equal lengths of the Te−O show four normal vibrations. Two of them υ (A1) and υ (E) correspond to the symmetric (υ^s) and degenerate (v^d). The polyhedra are assigned to the point group C_{3v} [20,21].

The infrared transmission spectrum of glasses in $TaO_{2.5}$ −TeO_2 system (Figure 5) exhibits vibrational bands in the range 600−800cm^{-1}. This region may also consist of bands due to anti-symmetrical and symmetrical vibrations of TeO_2. For (5% $TaO_{2.5}$ content) an intense band is observed nearly at 671cm^{-1} when compared with crystal (TeO_2). It characterizes the presence of non-symmetrical TeO_4 groups which give an indication

that tellurium does not change its coordination number four in this range of compositions. This band 671cm^{-1} is attributed to the asymmetric vibrations in O_{ax}−Te−O_{ax} groups into TeO_4 polyhedra. It is progressively broadening and moving towards the higher energy with $TaO_{2.5}$ content, which is the characteristic of more distortions of TeO_4 polyhedra. The second band (shoulder) (nearly observed at 780cm^{-1}) was attributed to asymmetrical vibrations of TeO_4 structural units (O_{eq}−Te−O_{eq}). The presence of mainly TeO_{3+1} and TeO_3 entities is the signature of breaking off in the tellurite matrix glass network due to a large proportion of added tantal oxide.

The two modes observed nearly at 780 and 671cm−1 canbe assigned as the frequency shifts from υ_1(A1) = $\upsilon^s(TeO4)_{eq}$ = 780cm^{-1} and υ_2(A1) = 650cm^{-1} with the formation of TeO_3 units. The downward shift of the $\upsilon s(TeO_4)_{eq}$ and $\upsilon s(TeO_4)$ax modes in the spectra of the binary TeO_2−MO (or M_2O) systems have been reported in the literature [17-20]. According to Dimitrova- Pankova et al. [17] TeO_{3+1} structural units are formed in binary tellurite glasses containing monovalent or bivalent cations as network modifiers. For 10 mol% $TaO_{2.5}$ we observe tow bands (662-770 cm^{-1}). With increasing modifier content, the deformation of the TeO_4 polyhedra became greater, and the symmetry of the TeO_4 group decreases.

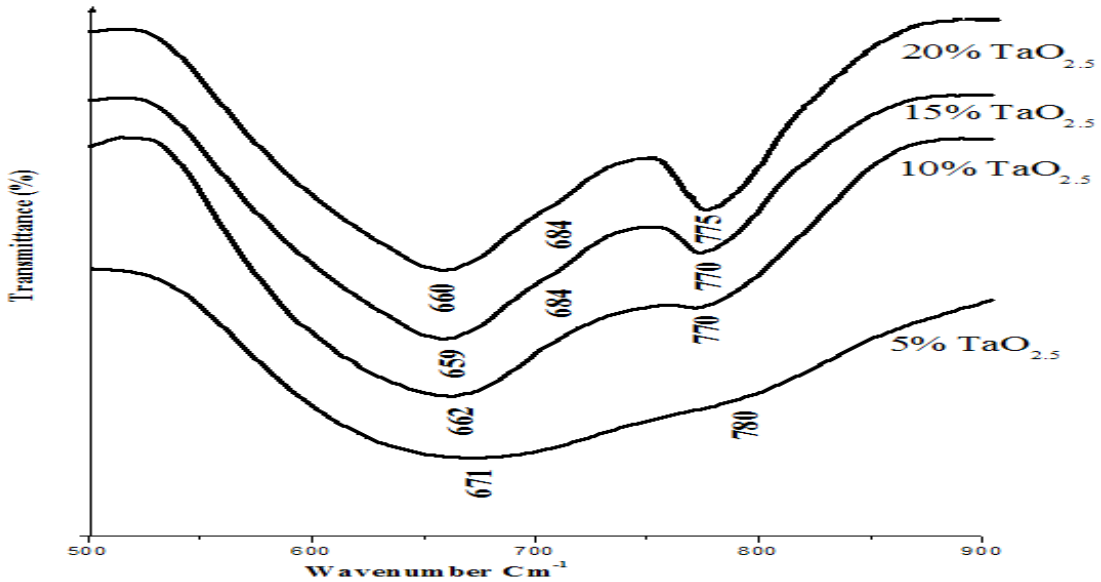

Figure 5: IR transmission spectra of glasses and crystalline phases of the TeO_2 - $TaO_{2.5}$ system.

3.3.2 Raman spectra

The Raman spectra of the pseudo binary TeO_2-$TaO_{2.5}$ vitreous phases versus the added amount of $TaO_{2.5}$ is illustrated in (Figure 6). For all samples, spectra obtained from different spots are identical showing high homogeneity of glasses. As shown in (Figure 6), there are two pronouncing peaks occur around 670–690 cm^{-1} and 750–770 cm^{-1}. The most prominent band at 680 cm^{-1} in the spectrum of pure glass is related to the combined vibrations of asymmetric stretching of Te-eqOax-Te bonds and symmetric stretching of TeO_4 (TBP). With addition of $TaO_{2.5}$ up 20 % mol fraction, intensity of this band decreases (G_1), while bands at 750–770 cm^{-1} (G_2) attributed to stretching vibrations of non-bridging Te-O- bands in TeO3 (TP). The peak (G_2), which is assigned to a stretching vibration of TeO_4 units, was observed to decrease as the $TaO_{2.5}$ contents increases. The decrease in intensity would suggest the possibility of conversion from TeO_4 tbp units to the other basic structural unit [22]. The peak (G_1) is reported to be due to the perturbation of TeO_4 (TBP) units into TeO_3 (trigonal pyramids) units via the intermediate coordination of TeO_{3+1} [22- 24]. Both features would clearly indicate that the network of the TeO_3 structural unit increases with the increasing of $TaO_{2.5}$ contents. Other peaks around (P) 350-550 cm^{-1}, are observed to be less sensitive to the $TaO_{2.5}$ contents. A decrease in

the peak intensity would suggest the occurrence of the destruction of Te–O–Te (or O–Te–O) in the linkages, thus resulted in the decreasing of the Te–O–Te linkages in a continue network of TeO_n (n = 4, 3 + 1, or 3) entities, which is consistent with the observation reported elsewhere [24], the intensity of this band decreases, while bands at 680 and 760 cm^{-1} were attributed to stretching vibrations of non-bridging Te–O– bands in TeO_3 (TP) grow in intensity. An other peaks around 50 cm^{-1} occur in all glasses is assigned to Boson. The orthotellurate ion, TeO_6^{6-}, will have octahedral symmetry but may be strongly distorted. Vibrational modes for the tellurate anion should occur in the 620–650 cm^{-1} and in the 290–360 cm^{-1} regions [25].

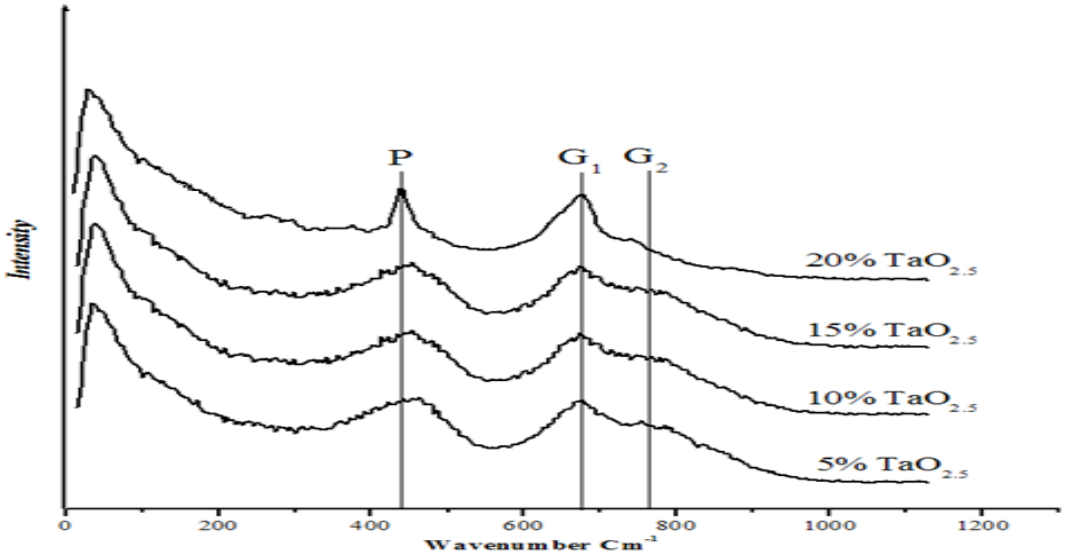

Figure 6: Raman spectra of glasses and crystalline phases of the $TaO_{2.5}$–TeO_2 system.

Conclusion

A stable glass has been synthesized in Bi_2O_3–Ta_2O_5–TeO_2 system at 850 ◦C. The vitreous crystallization of the samples rich of TeO_2 occurs for the αTeO2, γTeO_2 and $Ta_2Te_3O_{11}$ polymorphs. The γTeO_2 variety transforms complete to αTeO_2 up 550°C.

The X ray diffraction spectra of the crystallized phases gained after a thermal annealing of the composition 85 % TeO_2 15% $TaO_{2.5}$ at a temperature of 500 °C during 24h, shows the existence of a tri-phased mixture TeO_2 (α), TeO_2 (γ) and a new phase called Y.

The densities and molar volume of the glasses decrease in $TaO_{2.5}$ content. The characteristic temperatures (glass transition and crystallization temperatures) have been determined.

The influence of a gradual addition of the modifier oxides on the coordination geometry of tellurium atoms has been elucidated. Based on IR absorption curves and the Raman spectra of glasses show systematic changesin structural units, from TeO_4 trigonal bipyramid (tbps) to TeO_3 trigonal pyramid (tps) via [TeO_{3+1}] entities with increasing $TaO_{2.5}$ content in glass.

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