Synthesis and characterization of new amorphous and crystalline phases in Bi$_2$O$_3$-Ta$_2$O$_5$-TeO$_2$ system

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Abstract
A glass-forming domain is found and studied within Bi$_2$O$_3$–Ta$_2$O$_5$–TeO$_2$ system. The glasses obtained in the system Ta$_2$O$_5$–TeO$_2$ was investigated by DSC, Raman and Infrared spectroscopy. The influence of a gradual addition of the modifier oxides Ta$_2$O$_5$ on the coordination geometry of tellurium atoms has been elucidated based on infrared and Raman studies and showed the transition of TeO$_4$, TeO$_{3+1}$ and TeO$_3$ units with increasing Ta$_2$O$_5$ content. The density of glasses has been measured. The investigation in the TeO$_2$–Ta$_2$O$_5$ 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 switches 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 make the 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$_2$O$_5$, TeO$_2$–Nb$_2$O$_5$–ZnO, TeO$_2$–Bi$_2$O$_3$–ZnO, TeO$_2$–TiO$_2$–BaO, TeO$_2$–TiO$_2$–Bi$_2$O$_3$ and TeO$_2$–TiO$_2$–Nb$_2$O$_5$ 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$_2$O$_3$–Ta$_2$O$_5$–TeO$_2$ system. Elaboration process, thermal properties infrared (IR) and Raman 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$_2$O$_3$, TeO$_2$, Ta$_2$O$_5$ 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 Bi₂O₃-Ta₂O₅-TeO₂ system was prepared at 800°C after a series of composition. the vitreous was determined by X-ray diffraction . This temperature have been chosen to have a homogenous reagent in one hand and to avoid volatization of TeO₂ 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 Ta₂O₅ and Bi₂O₃ concentration.

![Figure 1: Vitreous domain diagram for the Bi₂O₃-TeO₂-Ta₂O₅ system](image)

3.1. Differential scanning calorimetry (DSC)

Series of glasses composition are listed in (Table 1). An addition of TaO₂.₅ (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 Ta⁵⁺ in the glass network. The values of Tg, Tc₁, Tc₂ and Tc₃ are presented (Figure 2) and (Table 1).
The curves (DSC) exhibit an endothermic effect due to glass transition (Tg), and shows that tree exothermic phenomenon occurred at (Tc₁), (Tc₂) and (Tc₃), due to the formation of different crystalline phases. The appearance of single peak (all glasses) due the glass transition temperature Tg indicates the homogeneity of the glasses prepared. With increasing of Ta₂O₅ 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 Ta₂O₅ 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 % TaO₂.5 (Figure 3a). The first peak of crystallization corresponds to the γTeO₂, αTeO₂ and Ta₂Te₃O₁₁ at 500°C. This phenomenon which we observed, i.e. the crystallization of γ TeO₂ variety is also obtained in the many systems as TeO₂-WO₃ [10], Nb₂O₅-TeO₂ [8,11], TeO₂-ZnO [12], TeO₂-SrO [13] and Sb₂O₃-TeO₂ [14]. In second crystallization at 550°C belongs to reinforcing Ta₂Te₃O₁₁ and αTeO₂ phases. The last peak (650°C) with weak intensity is attributed to totally transformation γTeO₂ metastable polymorph into the stable αTeO₂ and Ta₂Te₃O₁₁.

Table 1: Characteristics (Tg, Tc) and difference (Tc₁ - Tg) of some glasses in the Ta₂O₅–TeO₂–Bi₂O₃ system.

<table>
<thead>
<tr>
<th>%TeO₂</th>
<th>%TaO₂.5</th>
<th>Tg (°C)</th>
<th>Tc₁ (°C)</th>
<th>Tc₂ (°C)</th>
<th>Tc₃ (°C)</th>
<th>Tc₁-Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>5</td>
<td>378</td>
<td>490</td>
<td>522</td>
<td>595</td>
<td>112</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>380</td>
<td>412</td>
<td>518</td>
<td>572</td>
<td>38</td>
</tr>
<tr>
<td>85</td>
<td>15</td>
<td>382</td>
<td>461</td>
<td>516</td>
<td>576</td>
<td>79</td>
</tr>
</tbody>
</table>

Figure 2: DSC curves of glassy samples obtained in xTaO₂.5, (1-x)TeO₂ pseudo- binary (0.05≤x≤0.15)
It is important to mention that the thermal analysis curves discussed in paragraph 3-1 of glasses of the pseudo-binary TeO\textsubscript{2} – TaO\textsubscript{2.5} which have a composition of 15 % mol of TaO\textsubscript{2.5} exhibit three crystallizations, these 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\textsubscript{2}, 15% TaO\textsubscript{2.5}) at temperature 500 °C during 24h, shows the existence of a tri-phases mixture: TeO\textsubscript{2}(\alpha), TeO\textsubscript{2}(\beta) 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\textsubscript{2}(\alpha) and TeO\textsubscript{2}(\gamma) 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, $\beta=100.54^\circ$ and $V_{\text{lattice}} = 398.94$ Å$^3$. The reflection conditions are in agreement with space groups $C_c$ and $C_{2c}$. 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$_{2.5}$. 

3.2. Density and molar volume

3.2.1. Experiment procedure

The density of the specimens was measured using Archimedes principle using orthophtalate as the immersion liquid \((d_{\text{orthophtalate}} = 1.11573 \text{ at } 23.5^\circ\text{C})\). 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]:

\[
d = d_{\text{orthophtalate}} \left( \frac{W_{\text{air}}}{W_{\text{orthophtalate}}} \right)
\]

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 \((M_{\text{TaO}_{2.5}} > M_{\text{TeO}_2})\). 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$_{2.5}$

<table>
<thead>
<tr>
<th>%mol TeO$_2$</th>
<th>% mol TaO$_{2.5}$</th>
<th>Density ($\pm$0.02)</th>
<th>molar volume (M)$({\text{Å}}^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>5</td>
<td>6.10</td>
<td>26.67</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>6.25</td>
<td>26.49</td>
</tr>
<tr>
<td>85</td>
<td>15</td>
<td>6.41</td>
<td>26.33</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>6.57</td>
<td>26.15</td>
</tr>
</tbody>
</table>

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:

$\nu$ (Te-O$_{eq}$) = 780 cm$^{-1}$, $\nu$ (Te-O$_{eq}$$^a$s) = 714 cm$^{-1}$, $\nu$ (Te-O$_{as}$) = 675 cm$^{-1}$ et $\nu$ (Te-O$_{ax}$) = 635 cm$^{-1}$.

In the pure TeO$_2$ glass the $\nu^s$ band at 635 cm$^{-1}$ increases markedly instated of $\nu^a$ TeO$_{ax}$ = 675 cm$^{-1}$ and becomes a determining one. The rise of $\nu_{ax}$ 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 $\nu$ (A1) and $\nu$ (E) correspond to the symmetric ($\nu^s$) and degenerate ($\nu^d$). 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 600–800 cm$^{-1}$. 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 671 cm$^{-1}$ 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 671 cm\(^{-1}\) 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 780 cm\(^{-1}\)) 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 671 cm\(^{-1}\) can be assigned as the frequency shifts from \(v_1(A1) = v'(TeO_4)_{eq} = 780 \text{ cm}^{-1}\) and \(v_2(A1) = 650 \text{ cm}^{-1}\) with the formation of TeO\(_3\) units. The downward shift of the \(v_1'(TeO_4)_{eq}\) and \(v_2'(TeO_4)_{ax}\) modes in the spectra of the binary TeO\(_2\)-MO (or M\(_2\)O) 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 two 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.

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 TeO\(_3\) (TP). The peak (G\(_2\)), which is assigned to a stretching vibration of TeO\(_3\) units, was observed to decrease as the TaO\(_{2.5}\) contents increases. The decrease in intensity would suggest the possibility of conversion from TeO\(_4\) tshp 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 TeO₃ (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 TeO₃ (TP) grow in intensity. An other peaks around 50 cm⁻¹ occur in all glasses is assigned to Boson. The orthotellurate ion, TeO₆⁻, 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 TaO₂.5–TeO₂ system.](image)

Conclusion

A stable glass has been synthesized in Bi₂O₃–Ta₂O₅–TeO₂ system at 850 °C. The vitreous crystallization of the samples rich of TeO₂ occurs for the αTeO₂, γTeO₂ and Ta₂Te₃O₁₁ polymorphs. The γTeO₂ variety transforms complete to αTeO₂ up 550°C. The X ray diffraction spectra of the crystallized phases gained after a thermal annealing of the composition 85 % TeO₂ 15% TaO₂.5 at a temperature of 500 °C during 24h, shows the existence of a tri-phased mixture TeO₂ (α), TeO₂ (γ) and a new phase called Y.

The densities and molar volume of the glasses decrease in TaO₂.5 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 changes in structural units, from TeO₄ trigonal bipyramid (tbp) to TeO₃ trigonal pyramid (tps) via [TeO₃₋₁] entities with increasing TaO₂.5 content in glass.

References