

# Glass formation study within the $\text{TeO}_2$ –TlF and $\text{Tl}_2\text{Te}_3\text{O}_7$ –TlF systems

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**Abstract** – Large glassy domains have been observed at 800 °C within the  $\text{TeO}_2$ –TlF (from 7 to 65 mol% of TlF) and  $\text{Tl}_2\text{Te}_3\text{O}_7$ –TlF (from 0 to 75 mol% of TlF content) systems. The density, glass transition and crystallisation temperatures of glassy samples have been determined. The main features of a structural evolution within the TlF– $\text{TeO}_2$  glasses have been interpreted by analysing the relevant Raman spectra, and comparing them with those previously observed for the  $\text{Tl}_2\text{O}$ – $\text{TeO}_2$  system. **To cite this article:** C. Lasbruggas et al., C. R. Chimie 5 (2002) 607–611 © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

glasses / fluorotellurite / Raman scattering

**Résumé** – De larges domaines vitreux ont été mis en évidence à 800 °C au sein des systèmes pseudo-binaires  $\text{TeO}_2$ –TlF (de 7 à 65% en mole de TlF) et  $\text{Tl}_2\text{Te}_3\text{O}_7$ –TlF (de 0 à 75% en mole de TlF). Les masses volumiques, les températures de transition vitreuse et de cristallisation des verres ont été mesurées. Les principales modifications structurales des verres du système TlF– $\text{TeO}_2$  ont été analysées par diffusion raman en comparant les spectres obtenus avec ceux précédemment observés pour les verres du système  $\text{Tl}_2\text{O}$ – $\text{TeO}_2$ . **Pour citer cet article :** C. Lasbruggas et al., C. R. Chimie 5 (2002) 607–611 © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

verres / oxyfluorures de tellure / diffusion Raman

## 1. Introduction

The  $\text{TeO}_2$ -based glasses form a highly interesting field of recent studies aiming at basic scientific goals as well as research for new promising materials for non-linear optics. However, whereas the exceptional dielectric and optical properties of those materials are usually associated with the E-pairs of Te(IV), the nature of their mechanical and thermal properties remains an open question. Evidently, such properties must be related to the presence of the  $\text{Te}_{\text{eq}}\text{O}_{\text{ax}}\text{--Te}$  bridges, which always exist in the condensed  $\text{TeO}_2$ , and in tellurite structures, having complex  $\text{Te}_n\text{O}_m$  anions [1]. Those bridges, as a rule, are essentially

asymmetric, since the equatorial Te–O bonds are mainly covalent, and the axial ones are mainly electrostatic [2].

Thus, it can be thought that the properties in question can be controlled by the polymerisation (homogenisation) of the Te–O–Te bridges. In particular, this can be done by introducing the fluorine atoms into the coordination spheres of tellurium. In the cases of the Te–O–F system, the atoms of fluorine (being more electronegative than oxygens) would accept some electrons of tellurium, thus allowing each Te atom to form the two simple Te–O bonds [3], which can polymerise into the Te–O chains, having Te–O–Te bridges similar to Si–O–Si bridges. In those chains, the  $\text{TeO}_2$

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fragments can be readily distinguished, like the  $\text{SiO}_4$  units can be distinguished in the  $\text{SiO}_2$  framework.

Thus, whereas the pure tellurium dioxide systems would have quasi-isolated  $\text{TeO}_2$  units that cannot polymerise [4], it appears that the existence of polymerised Te–O chains is intrinsic for Te–O–F systems. Such a sharp difference in the electronic structure and crystal chemistry of those objects must be reflected on their fundamental physical properties. At present, a number of works have been devoted to the investigations of tellurium–oxyfluoride mixed systems [5–12].

Our previous study of the  $\text{TeO}_2$ – $\text{TeF}_4$  system has clearly shown the influence of F atoms as a factor enlarging the glass forming domain and favouring the structural evolution from a three-dimensional (but weakly polymerised) network ( $\text{TeO}_2$ ) into a well-pronounced chain-like one ( $\text{TeOF}_2$ ) via a sheet-like framework ( $\text{Te}_2\text{O}_3\text{F}_2$ ) [3, 13]. From these points of view, we are now investigating the  $\text{TeO}_2$ – $\text{Tl}_2\text{O}$ –TIF system. Our previous study of the  $\text{TeO}_2$ – $\text{Tl}_2\text{O}$  system clearly demonstrated that non-linear refractive indices of thallium tellurite glasses could be up to 100 times as large as those of  $\text{SiO}_2$  and that increasing the thallium content leads to the transformation of  $\text{TeO}_4$  disphenoids into isolated  $\text{TeO}_3$  trigonal pyramids and to the decrease of the number of Te–O–Te linkages [14]. In this work, we have evidenced the glass-forming domain within the  $\text{TeO}_2$ –TIF and  $\text{Tl}_2\text{Te}_3\text{O}_7$ –TIF systems. The densities and the thermal behaviour of the glasses (glass transition and crystallisation temperatures) have been determined. A structural study of thallium fluorotellurite glasses has also been approached.

## 2. Experimental

Glassy samples were prepared by first melting at 800 °C for 20 min in sealed gold tubes and then air-quenching intimate mixtures of TIF (Aldrich, 99.9%) and  $\text{TeO}_2$  (for the study of the  $\text{TeO}_2$ –TIF system) or TIF and  $\text{Tl}_2\text{Te}_3\text{O}_7$  (for the study of the  $\text{Tl}_2\text{Te}_3\text{O}_7$ –TIF system).  $\text{TeO}_2$  was prepared by decomposition at 550 °C under flowing oxygen, of commercial  $\text{H}_6\text{TeO}_6$  (Aldrich).  $\text{Tl}_2\text{Te}_3\text{O}_7$  was obtained by heating, at 350 °C for 18 h then at 250 °C for 24 h, in a gold crucible under pure flowing nitrogen, various mixtures of high purity  $\text{Tl}_2\text{CO}_3$  (Aldrich, 99%) and  $\text{TeO}_2$ . Glass-formation domains were determined by using X-ray diffraction (Guinier–De Wolff camera,  $\text{Cu K}\alpha$  radiation). Glass transition ( $T_g$ ) and crystallisation ( $T_c$ ) temperatures were measured by heat flux differential scanning calorimetry (Netsch STA 409). The powdered samples ( $\approx 30$  mg) were introduced into non-sealed platinum crucibles and the DSC curves were recorded between 20 and 800 °C maximum, using a

heating rate of 10 °C  $\text{min}^{-1}$ , under pure nitrogen atmosphere. The densities of glassy samples were measured on finely ground powders by helium pycnometry (Accupyc 1330). A structural approach of the glasses was realised using Raman scattering. The Raman spectra were recorded in the 80–1200  $\text{cm}^{-1}$  range using a Dilor spectrometer (XY model), equipped with a CCD detector and an  $\text{Ar}^+$  laser (514.5 nm exciting line) in a backscattering geometry. With such a detector, a good signal/noise ratio needed one or at most two scans (during 100 s). The samples were visually controlled through a microscope ( $\times 100$ ), which has enabled us to analyse a surface with diameter of about 2  $\mu\text{m}$ . The diameter of the laser spot focused on the sample was about 1  $\mu\text{m}$ . Reproducibility of the results thus obtained was a proof of identity and homogeneity of the samples. Measurements were made at low power ( $< 100$  mW) of the excitation line, in order to avoid any damage of the samples. The spectral resolution was about 4.5  $\text{cm}^{-1}$  at the exciting line.

## 3. Results and discussion

### 3.1. Formation and thermal behaviour of glasses

Under our experimental conditions, melting at 800 °C and then air quenching, large glassy domains have been evidenced within the  $\text{TeO}_2$ –TIF (from 7 to 65 mol% of TIF) and  $\text{Tl}_2\text{Te}_3\text{O}_7$ –TIF (from 0 to 75 mol% of TIF content) pseudo-binary systems (Fig. 1). With respect to the glassy domain observed within the  $\text{TeO}_2$ – $\text{Tl}_2\text{O}$  system [15] under the same conditions of elaboration, 15 to 52 mol% of  $\text{TlO}_{0.5}$ , it is clearly seen that addition of F atoms allows enlarging the glass-forming domain. Within the  $\text{TeO}_2$ –TIF system, the glasses are all homogeneous and white;

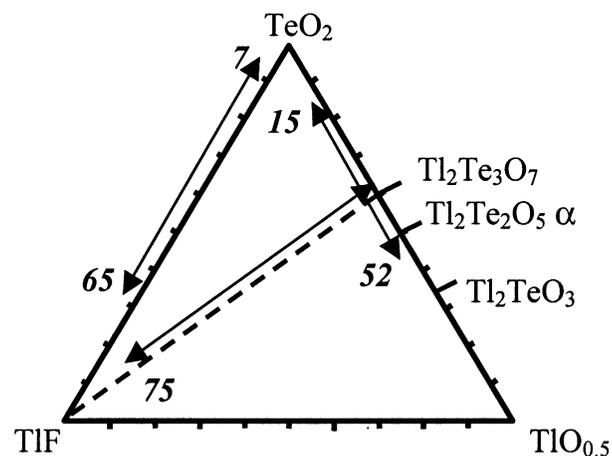


Fig. 1. Glass-forming domains within the  $\text{TeO}_2$ – $\text{Tl}_2\text{O}$ ,  $\text{TeO}_2$ –TIF and  $\text{Tl}_2\text{Te}_3\text{O}_7$ –TIF systems.

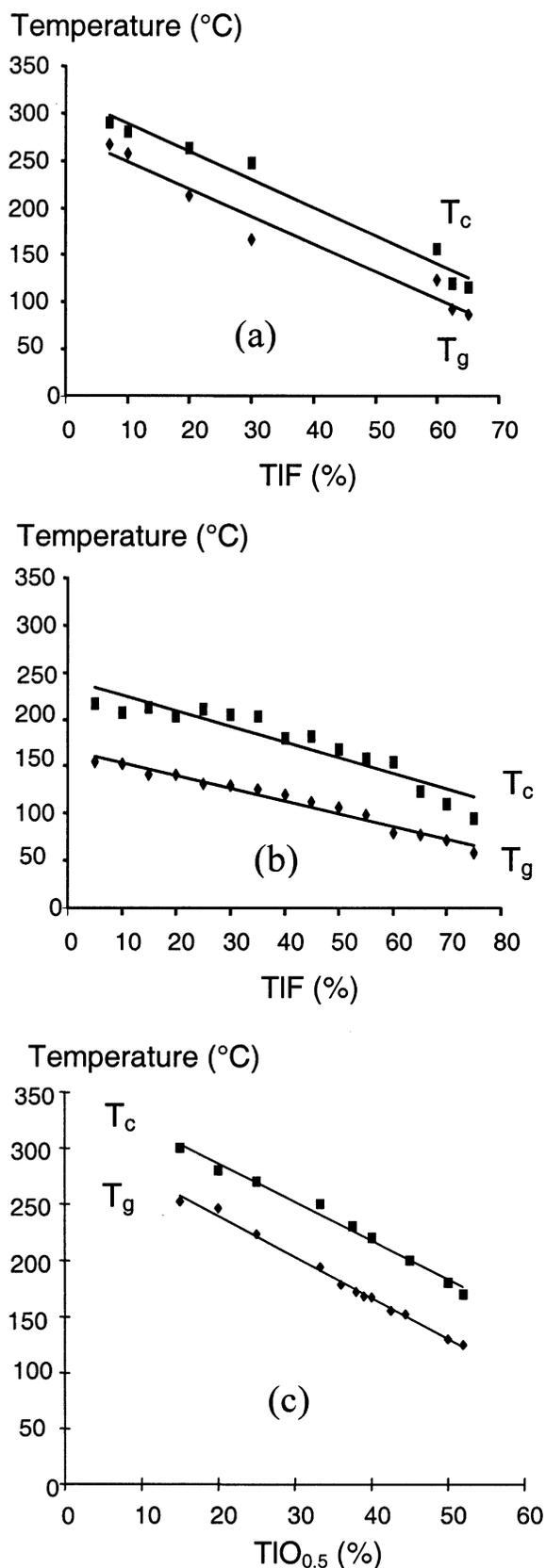


Fig. 2. Evolutions with composition of the glass transition ( $T_g$ ) and crystallisation ( $T_c$ ) temperatures within the (a)  $\text{TeO}_2$ -TIF, (b)  $\text{Te}_2\text{Te}_3\text{O}_7$ -TIF and (c)  $\text{TeO}_2$ - $\text{Ti}_2\text{O}$  systems.

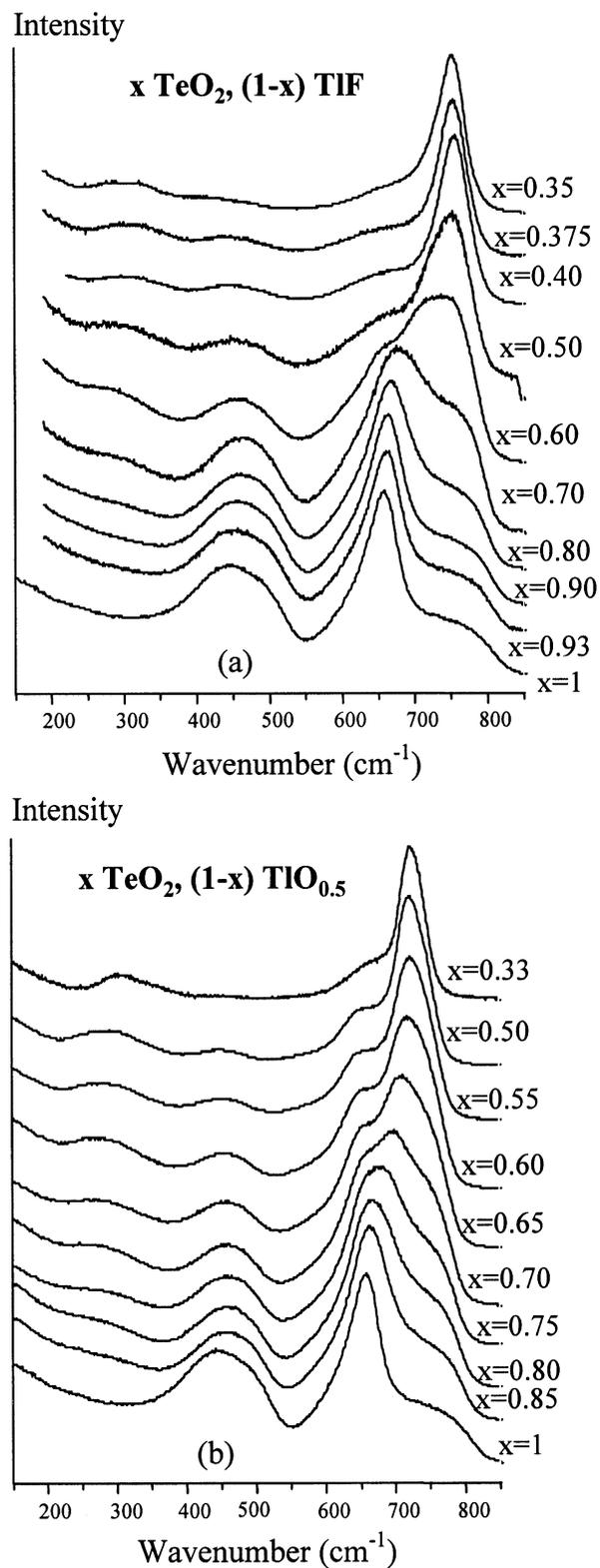


Fig. 3. Raman spectra of (a)  $\text{TeO}_2$ -TIF glasses and (b)  $\text{TeO}_2$ - $\text{Tl}_2\text{O}$  glasses (for the latter system, the glassy domain has been extended from 0 mol%  $\text{TlO}_{0.5}$  up to 66.7 mol%  $\text{TlO}_{0.5}$  under the extreme conditions of first melting at 800  $^{\circ}\text{C}$  and then ice quenching).

their density increases from 5.7 to 7.06 g cm<sup>-3</sup> with increasing the TIF content. Within the Tl<sub>2</sub>Te<sub>3</sub>O<sub>7</sub>-TIF system, the glasses are also homogeneous. Their colour changes from yellow to white with increasing the TIF content; their density increases from 6.72 to 7.21 g cm<sup>-3</sup> with increasing the TIF content. The evolutions within these two systems of the glass transition and crystallisation temperatures, as a function of the composition, are shown in Fig. 2. As a comparison, the evolution observed with TeO<sub>2</sub>-Tl<sub>2</sub>O glasses is also given.

Within our two fluorotellurite systems,  $T_g$  and  $T_c$  temperatures continuously decrease with increasing the TIF content, as previously observed with increasing the TiO<sub>0.5</sub> content. This decrease can be attributed to the thallium addition. It is interesting to note that the difference between  $T_c$  and  $T_g$ , which characterises the thermal stability of the glass, remains practically constant with increasing TIF content (for all the compositional range within the TeO<sub>2</sub>-TIF system and at least up to about 65 mol% of TIF within the Tl<sub>2</sub>Te<sub>3</sub>O<sub>7</sub>-TIF system). However, the thermal stability of TeO<sub>2</sub>-TIF glasses is slightly lower than that observed with thallium tellurite glasses. This can indicate that the substitution of O atoms by F ones would decrease the thermal stability of glassy samples. Above 60 mol% of TIF content, Tl<sub>2</sub>Te<sub>3</sub>O<sub>7</sub>-TIF glasses are characterised by a sharp decrease of their  $T_c$  temperature, whereas their  $T_g$  temperature decreases slowly, thus reducing their thermal stability. However, such glasses exhibit a thermal stability in the range 55–95 °C considerably superior to that of TeO<sub>2</sub>-TIF ones. A study of the crystallisation (especially the nature of the first phase that crystallises from glass) of such samples is now in progress using in-situ powder XRD. Preliminary results have confirmed the existence of the metastable  $\gamma$ -TeO<sub>2</sub> polymorph [4,16] for TeO<sub>2</sub>-rich samples.

### 3.2. Structural aspects of the TeO<sub>2</sub>-TIF glasses

The structural aspects of our study were mainly considered by analysing the evolution of the Raman spectra of the  $x$  TeO<sub>2</sub>/(1 -  $x$ ) TIF system ( $0.35 \leq x \leq 1$ ), and comparing it with that of the  $x$  TeO<sub>2</sub>/(1 -  $x$ ) TiO<sub>0.5</sub> system. Raman spectra of the latter (Fig. 3b) show that with decreasing  $x$ , the solid TeO<sub>2</sub> continuously evolves into the Tl<sub>2</sub>TeO<sub>3</sub> system, in which all the TeO<sub>2</sub> molecules become the isolated [TeO<sub>3</sub>]<sup>2-</sup> orthoanions having the two principal vibrations: a stretching pulsation (near 725 cm<sup>-1</sup>) and a symmetric bonding of the TeO<sub>3</sub> pyramids ( $\approx 300$  cm<sup>-1</sup>). Another type of structural evolution can be proposed from the analysis of the Raman spectra of the  $x$  TeO<sub>2</sub>/(1 -  $x$ ) TIF system. Actually, for  $0.6 \leq x \leq 1$ , the Raman spectrum keeps its view typical for (pure) glassy TeO<sub>2</sub>. Beginning from  $x = 0.6$ , the quantity of glassy TeO<sub>2</sub> sharply drops: the intense band near 450 cm<sup>-1</sup> (indicating Te-O-Te bridges) disappears, and a strong band appears above 750 cm<sup>-1</sup>, which indicates the formation of isolated groups having short (essentially non-bridging) Te-O bonds; a very weak band around 300 cm<sup>-1</sup> can be attributed to the bonding vibrations of O-Te-O angles.

Thus, no indication of the Te-O chains (i.e. Te-O-Te polymerisation) was observed in the Raman spectra. This fact could be explained by the presence of Tl<sup>+</sup> cations. To our belief, for  $0.6 \leq x \leq 1$ , the two phases, TIF and TeO<sub>2</sub>, coexist in the glasses independently. The mutual influence begins when  $x \leq 0.6$ , and it results in a reaction of TeO<sub>2</sub> molecules with fluorine atoms, thus forming isolated groups containing non-bridging Te-O bonds. The concrete structure of those groups will be the object of our further XRD study of the relevant crystalline phases.

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