New fluorotellurite glasses within the TeO_2-Tl_2O-TlF system.

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Large glassy domains have been observed at 800°C within the TeO_2-TlF (from 7 to 65 mol% of TlF) and $Tl_2Te_3O_7$-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-TeO_2 glasses have been interpretated by analysing the relevant Raman spectra, and comparing them with those previously observed for the TlO-TeO_2 system.

Introduction

Whereas the exceptional dielectric and optical properties of TeO_2 (and related) glasses are usually associated with the E-pairs of Te(IV), the mechanical and thermal properties of those glasses, evidently, must be governed by the short-range interactions between the “elementary” TeO_n structural units. These interactions can be described in terms of the Te-eqOax-Te bridges which always exist in the condensed TeO_2, and in tellurite structures having complex Te_nO_m anions ($n \geq 2$). Those bridges, as a rule, are essentially asymmetric since the equatorial Te-O bonds are mainly covalent, and the axial ones are mainly electrostatic, the bond order of the former bonds in paratellurite (α-TeO_2) being five times greater than that on the latter bonds. This fact allows us to speak about the TeO_2 quasi-molecules as basic structural units in TeO_2 and tellurites[1,2,3]. It appears, that the Te-O bonds in those molecules are “over saturated” by electrons and therefore such bonds can not polymerise and form Te-O-Te bridges similar to Si-O-Si ones in SiO_2 and silicates. Actually, the Te-O bonds in such bridges must be “ordinary” (i.e. simple), to provide the existence of an electron octet around O-atoms. It is highly likely, that this point is a central one in understanding the crystal chemistry of TeO_2 and “classical” tellurites. When fluor atoms are introduced into such a structure, the two F atoms can approach each TeO_2 molecule and (being more electronegative than O) form the $TeOF_2$ units. This would allow to each Te to form the two simple Te-O bonds with neighbouring oxygen atoms. Those would necessary polymerise into the Te-O chains, having the Te-O-Te bridges similar to Si-O-Si bridges. In those chains, the TeO_2 units can be readily distinguished like the SiO_4 units can be distinguished in SiO_2 framework. Thus, whereas the pure tellurium dioxide (and related) systems would have the TeO_4 units which can not polymerise, it appears that the existence of polymerised Te-O chains is intrinsic for F-Te-O systems. To our opinion, such a sharp difference in the electronic structure and crystal chemistry of those objects must be reflected on their fundamental physical properties. This seems to us highly interesting field of relevant studies aiming at the basic scientific goals as well as the researches of new promising materials for non-linear optics.

A previous study of the TeO_2-TeF_4 system has clearly shown the influence of F atoms which allow to enlarge the glass forming domain and favours the structural evolution from a three-dimensional network (TeO_2) into a chains-like one ($TeOF_2$) via a sheets-like framework ($Te_2O_3F_2$)[4,5]. From these points of view, we are now investigating the TeO_2-Tl_2O-TlF system. Our previous study at the TeO_2-Tl_2O system clearly demonstrated that non linear refractive indices of thallium tellurite glasses could be up to 100 times as large as that of SiO_2 and that increasing thallium content leads to the transformation of TeO_4 disphenoids into isolated TeO_3 trigonal pyramids and to the decrease of the number of Te-O-Te linkages[6]. In this work we have evidenced the glass forming domain within the TeO_2-TlF and $Tl_2Te_3O_7$-TlF 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.

Experimental

Glassy samples were prepared by first melting at 800 °C for 20 minutes in sealed gold tubes, and then air – quenching, intimate mixtures of TlF (Aldrich, 99.9%) and TeO_2 (for the study of the TeO_2-TlF system) or TlF and $Tl_2Te_3O_7$ (for the study of the $Tl_2Te_3O_7$-TlF system). TeO_2 was prepared by decomposition at 550 °C under flowing oxygen, of commercial H_6TeO_6 (Aldrich). $Tl_2Te_3O_7$ 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 Tl_2CO_3 (Aldrich, 99%) and TeO_2. Glass formation domains were determined by using X-ray diffraction (Guinier – De Wolff camera, Cu - $K\alpha$ radiation). Glass transition (Tg) and crystallisation (Tc) 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 min^{-1} and 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 diffusion. The raman spectra were recorded in the 80-1200 cm^{-1} range using a Dilor spectrometer (XY model) equipped with a CCD detector and an 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 (×100), which had enabled us to analyse a surface with diameter of about 2 µm. The diameter of the laser spot focused on the sample was about 1 µm. 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 cm^{-1} at the exciting line.

Results and discussion

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 TeO_2-TlF (from 7 to 65 mol% of TlF) and $Tl_2Te_3O_7$-TlF (from 0 to 75 mol% of TlF content) pseudo binary systems (figure 1). With respect to the glassy domain observed within the TeO_2-Tl_2O system[7] under the same conditions of elaboration, 15 to 52 mol% of $TlO_{0.5}$, it is clearly seen that addition of F atoms allows to enlarge the glass forming domain. Within the TeO_2-TlF system, the glasses are all homogeneous and white, their density increases from 5.7 g/cm^3 to 7.06 g/cm^3 with increasing TlF content. Within the $Tl_2Te_3O_7$-TlF system, the glasses are also homogeneous. Their colour changes from yellow to white with increasing TlF content and their density increases from 6.72 g/cm^3 to 7.21 g/cm^3 with increasing TlF content. The evolutions within these two systems of the glass transition and crystallisation temperatures, as a function of the composition, are shown in figure 2. As a comparison, the evolution observed with TeO_2-Tl_2O glasses is also given.

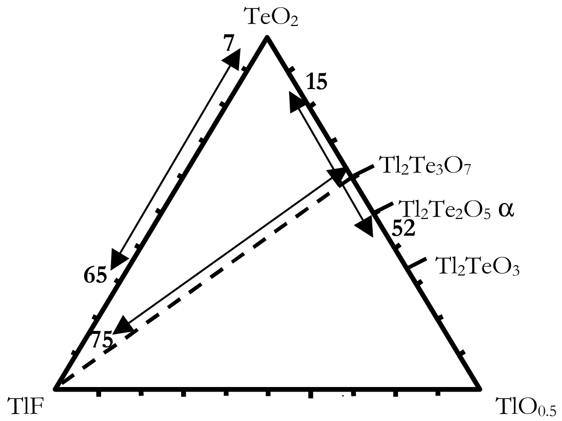

Figure 1: Glass forming domains within the TeO_2-Tl_2O, TeO_2-TlF and $Tl_2Te_3O_7$-TlF systems

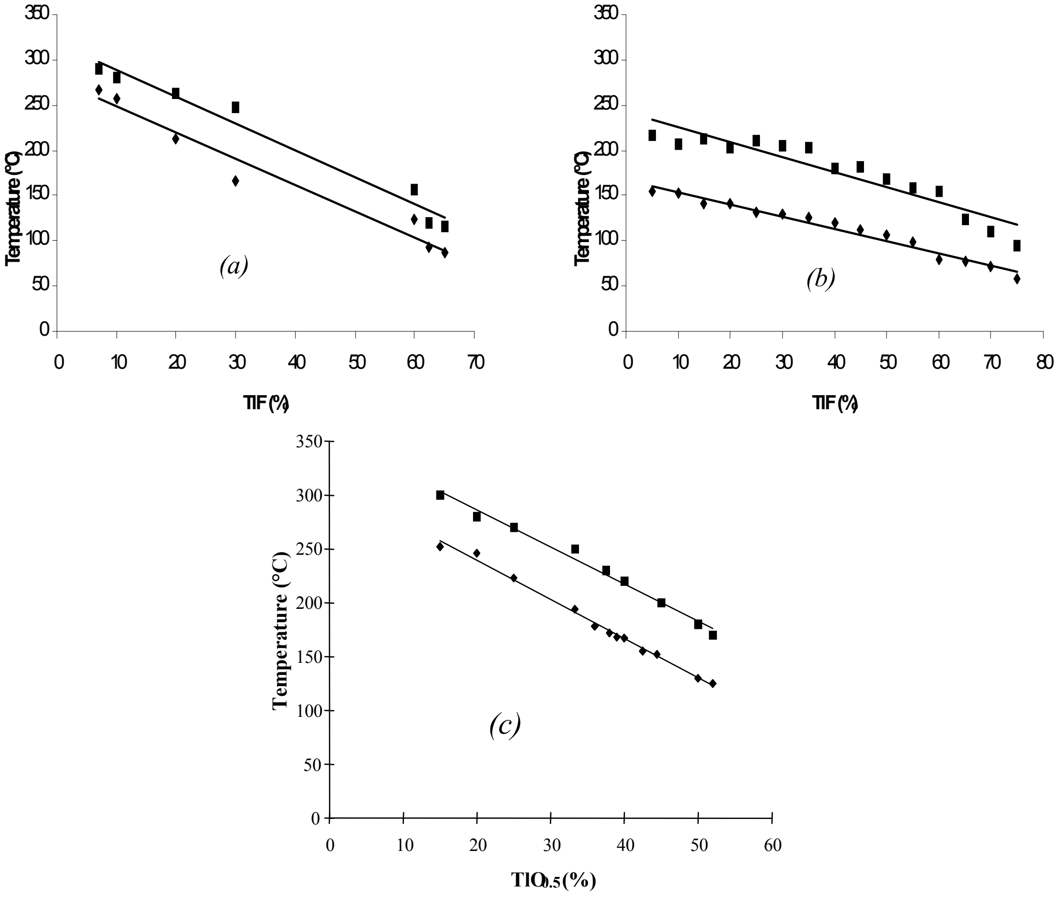

Figure 2: Evolutions with composition of the glass transition (Tg) and crystallisation (Tc) temperatures within the *(a)* TeO_2-TlF, *(b)* $Tl_2Te_3O_7$-TlF and *(c)* TeO_2-Tl_2O systems

Within our two fluorotellurite systems, Tg and Tc temperatures continuously decrease with increasing TlF content as previously observed with increasing $TlO_{0.5}$ content. This decrease can be attributed to the thallium addition. It is interesting to note that the difference between Tc and Tg, which characterises the thermal stability of the glass, remains practically constant with increasing TlF content (for all the compositional range within the TeO_2-TlF system and at least up to about 65 mol% of TlF within the $Tl_2Te_3O_7$-TlF system). However the thermal stability of TeO_2-TlF 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 TlF content, $Tl_2Te_3O_7$-TlF glasses are characterised by a sharp decrease of their Tc temperature whereas their Tg 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_2-TlF ones. A study of the crystallisation (especially the nature of the first phase which crystallise from glass) of such samples is now in progress using in-situ powder XRD. Preliminary results have confirmed the existence of the metastable γ-TeO_2 polymorph[1,2] for rich-TeO_2 samples.

Structural approach of the TeO_2-TlF glasses

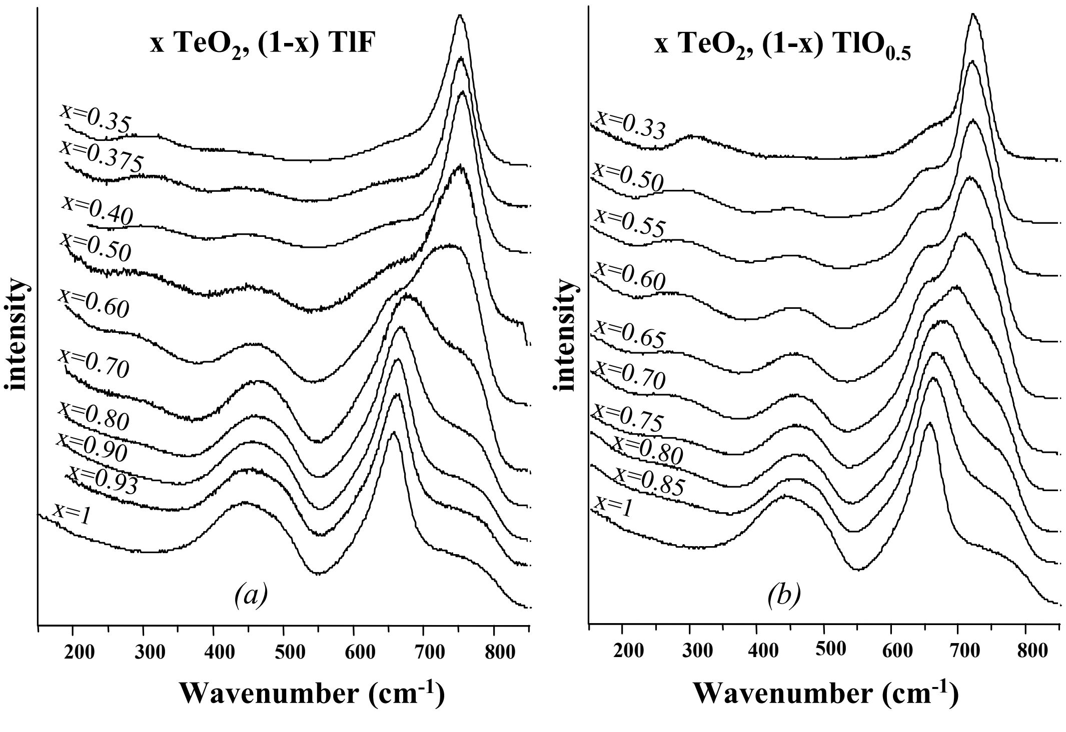

Figure 3: Raman spectra of *(a)* TeO_2-TlF glasses and *(b)* TeO_2-Tl_2O glasses (for the latter system, the glassy domain has been extended from 0 mol% $TlO_{0.5}$ up to 66.7 mol% $TlO_{0.5}$ under the extreme conditions of first melting at 800°C and then ice-quenching)

The structural aspects of our study were mainly related to the evolution of the Raman spectra of the xTeO_2-(1-x)TlF system with the x value variation, and its comparison with that of the xTeO_2-(1-x)Tl_2O system. Raman spectra of the latter (figure 2b) show that with decreasing x the solid TeO_2 consisting of the condensed TeO_2 molecules *continuously* evaluate into the Tl_2TeO_3 system in which all the TeO_2 molecules become the isolated $[TeO_3]^{2-}$ orthoanions having the two principal vibrations: a stretching pulsation (near 725 cm^{-1}) and a symmetric bonding of the TeO_3 pyramids (≈300 cm^{-1}). The other type of the structural evolution can be proposed from the analysis of the Raman spectra of the xTeO_2-(1-x)TlF system. Actually, for $0.7 \leq x \leq 1$, the Raman spectrum keeps its view typical for (pure) glassy TeO_2. Beginning from x= 0.6, the quantity of glassy TeO_2 sharply drops: the intense band near 450 cm^{-1} (indicating Te-O-Te bridges) disappears, and a strong band appears above 750 cm^{-1}, which indicates the formation of isolated groups having short (essentially non-bridging) Te-O bonds; a very weak band around 300 cm^{-1} 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) is found, which could be explained by the presence of the Tl^+ cations, and no Te-F (and Tl-F) stretching vibrations are observed in the Raman spectra. To our belief , for $0.7 \leq x \leq 1$, two subsystems, TlF and TeO_2, coexist in the glasses quite independently. The mutual influence begins when $x \leq 0.7$, and it results in a reaction of TeO_2 molecules with fluor atoms, thus forming isolated groups containing non-bridging Te-O bonds whose concrete structure can be established on a further XRD study of the relevant crystalline phases.

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