Structural study of TeO_2-M_yO_z (M=Ga, Sb, W) glasses

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Both the local structure and the nonlinear properties of glasses prepared in the TeO_2-M_yO_z (M=Ga, Sb or W) binary systems were investigated. Raman and Te L_{III} edge X-ray absorption spectra revealed that the addition of M_yO_z content to the glass former induces the transformation ot the glass network. Furthermore, the W, Sb and Ga environments were studied by ^{121}Sb Mössbauer and W L_I,L_{III} edge and Ga K edge XANES spectroscopies.

Introduction

TeO_2-based glasses have attracted much interest because of their high refractive index, dielectric constants, low dispersion, wide infrared transmission and high thermal expansion coefficients. In addition, some tellurite glasses were reported to be promising materials for use in non linear optical devices. Indeed, these glasses exhibit the highest nonlinear refractive indices n_2 ever found for oxide glasses[1-3]. In order to find a correlation between the physical properties and their atomic arrangement, structural characterizations and nolinear measurements were performed.

In the present work, we report the formation and the structural changes with composition of TeO_2-M_yO_z (M=Ga, Sb and W) binary glass systems. Raman, Mössbauer and X-ray absorption spectroscopies were used to study the local structure of these glass materials.

Experimentals

Synthesis

Transparent glass samples were prepared by melting mixtures of reagent grade α-TeO_2, α-Sb_2O_4, β-Ga_2O_3 and γ-WO_3 in an electric furnace heated up to 900 °C. The platinum crucible containing the melt was quickly quenched in an ice cold water bath. In order to extend the glass domain, some compositions were quenched in a freezing mixture (-10°C) consisting of ethanol, NaCl and ice. X-ray diffraction (Cu Kα) and differential scanning calorimetry (DSC) measurements were performed to confirm the glassy state. $(1-x)TeO_2$-xGa_2O_3 with $0 \leq x \leq 0.20$, $(1-x)TeO_2$-xSb_2O_4 with $0 \leq x \leq 0.175$ and $(1-x)TeO_2$-xWO_3 with $0 \leq x \leq 0.325$ glass compositions were synthetized.

Physical characterizations

Raman spectroscopy was performed using a LABRAM 1B confocal Raman spectrophotometer with an exciting He/Ne laser at 632 nm. The spectra recorded in the 1200-200 cm^{-1} wavenumber range at intervals of 1 cm^{-1}.

X-ray absorption spectra (XANES) were registered at LURE (Orsay, France) on the D44 beam line of the DCI storage ring operating at 1.85 GeV with an average positron current of 250 mA. Appropriate crystals were used as monochromator to obtain a single beam. The energy steps and the counting times were adjusted to improve data quality.

^{121}Sb and ^{125}Te Mössbauer spectra were carried out at LAMMI, Montpellier using respectively Ba^{121m}SnO$_3$ and Mg^{125m}TeO$_6$ compounds as Mössbauer sources. Source and absorber samples were held at liquid helium temperature (4.2K). The origin of the ^{121}Sb and ^{125}Te isomer shift scales were determined respectively from InSb and MgTe$_2$O$_6$ spectra.

Nonlinear measurements were performed by interferometry at CPMOH, Bordeaux. A Mach Zehnder interferometer compares two beams (probe and reference) in amplitude and phase. The laser used in this set-up is an OPO pumped by TiSa oscillator which delivers linearly polarized pulses around 0.8 μm and 1.5 μm.

Results and discussions

Raman spectroscopy has emerged as a powerful tool for the investigation of glass structure. It was used to study the vibration modes of the constituting polyhedra. Figure 1 shows the Raman spectra of (1-x)TeO$_2$-xSb$_2$O$_4$ glass samples with 0≤x≤0.175.

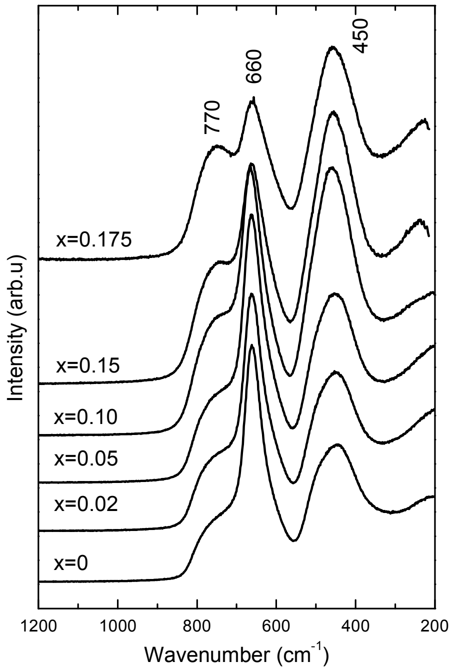

Figure 1 : Raman spectra of (1-x)TeO$_2$-xSb$_2$O$_4$ glasses with 0≤x≤0.175.

The main absorption frequencies in the 800-600 cm^{-1} range are assigned to stretching vibration modes of the Te-O bonds of TeO$_3$E and TeO$_4$E structural units. When the Sb$_2$O$_4$ content increases, the mode intensity at 660 cm^{-1} decreases while the feature at 770 cm^{-1} increases. This evolution, also registered for the TeO$_2$-Ga$_2$O$_3$ system, is an indication of the conversion of basic tellurite network units from trigonal bipyramids TeO$_4$E (660 cm^{-1}) into regular pyramids TeO$_3$E (770 cm^{-1}) units via an intermediate coordination called TeO$_{3+1}$E where one Te-O axial distance is elongated while the opposite is shortened (E = tellurium 5s^2 lone electronic pair)[4,5]. Concerning the TeO$_2$-WO$_3$ system, the tellurium atoms coordination can't be approached because of the overlap with the W-O vibrations in this range. The broad Raman peak around 450 cm^{-1} can be assigned to Te-O-M

(M=Ga, Sb, W) and Te-O-Te bridging bonds which stabilize glasses. A part of M cations have partial covalent bonding and are incorporated in the network.

Furthermore, ^{125}Te Mössbauer spectroscopy was performed coupled with a XANES study at Te L_{III} edge. ^{125}Te Mössbauer spectra are described by a doublet structure and characterized by two parameters, the isomer shift δ and the quadrupole splitting Δ. The isomer shift δ varies linearly with the electron density $\rho(0)$ at the Te nucleus which is mainly dependent on the s-type electrons. It decreases with the progressive transformation of TeO_4E units into TeO_3E units[6]. The quadrupole splitting Δ gives informations on the charge distribution around the Te atoms which can be related to the Te coordination and the chemical bonding. The XANES spectra exhibit a pre-peak assigned to $2p_{3/2} \rightarrow 5s$ transition. The intensity of this pre-peak depends on the coordination number of tellurium atoms. It increases gradually revealing a continuous change of tellurium atoms coordination number from 4 to 3 when the M_yO_z (M=Ga, Sb, W) content increases.

^{121}Sb Mössbauer spectroscopy and a XANES study at Sb L_I edge were performed to determine the Sb environment in TeO_2-Sb_2O_4 glasses. These revealed coexistence of Sb^{3+} and Sb^{5+} oxidation states involving mixed coordination of antimony (figure 2).

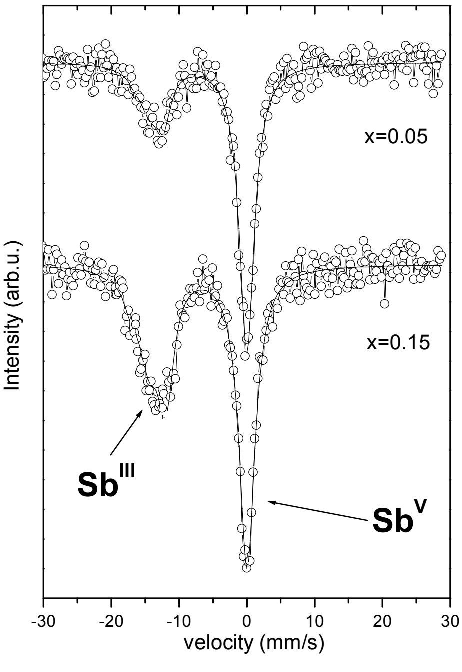

Figure 2 : ^{121}Sb Mössbauer spectra of (1-x)TeO_2-xSb_2O_4 glasses with x=0.05 and x=0.15.

Concerning TeO_2-Ga_2O_3 glasses, the Ga K edge XANES spectra of glasses present the same profile and are rather similar to the spectrum registered for the crystalline phase β-Ga_2O_3 : this similitude indicates the presence of mixed environment GaO_4 and GaO_6 in glasses as in β-Ga_2O_3[7]. In order to study the W environment in TeO_2-WO_3 glasses, W L_I and L_{III} edge XANES spectroscopy was used. For the L_{III} edge, the amplitude of the so-called "white line" resonance should reflect the local density of the d-state and the number of unoccupied 5d states[8]. For the L_I edge, we are interested in the pre-edge feature arising from the $2s \rightarrow 5d(W)+2p(O)$ transition determined by the site symmetry of the tungsten atoms (indexed A on figure 3)[9,10]. The transition is dipole forbidden in the case of regular octahedra (inversion center) but is allowed for distorted octahedra and tetrahedra. Compared to crystalline compounds, both W L_{III} and L_I XANES studies agree with the existence of W^{6+} ions in six fold coordination whatever the glass composition. Furthermore, the distortion of the WO_6 increases with the WO_3 content.

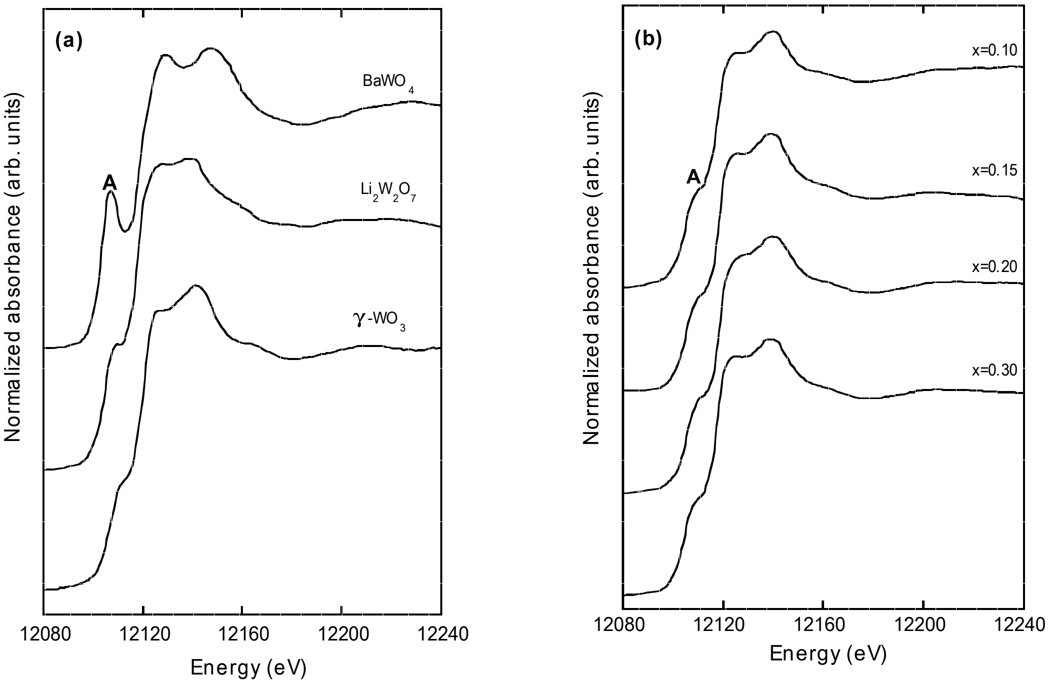

Figure 3 : Normalized W L_I edge XANES spectra of a) crystallized references $BaWO_4$, WO_3 and $Li_2W_2O_7$ and of b) $(1-x)TeO_2$-xWO_3 glasses.

The experimental values of nonlinear measurements depend on both the nature and the concentration of the cation introduced into the TeO_2 glassy matrix. The highest nonlinear susceptibilities χ^3 values were obtained for TeO_2-WO_3 glasses. This may be explained by the polarization of the transition ion having empty d orbitals and the influence of the electronic lone pair of tellurium. Very high nonlinear measurements are not obtained for the TeO_2-Sb_2O_4 system compared with other glasses containing highly hyperpolarisable ions such as Tl^+, Pb^{2+}, Te^{4+} and Bi^{3+} [11] having the same electronic configuration as Sb^{3+}. On an other hand, the addition of increasing quantities of modifying oxides to a TeO_2 glassy matrix with conversion of TeO_4E into TeO_3E units results in a decrease of χ^3 values.

Conclusion

Stable and transparent glasses were formed in the $(1-x)TeO_2$-xM_yO_z (M=Ga, Sb and W) glass systems. The structure of these glasses was investigated by means of Raman, Mössbauer and X-ray absorption spectroscopies. The mains structural results can be summarized as follows :

1-The coordination state of tellurium atoms changes in a gradual way from TeO_4E to $TeO_{3+1}E$ or TeO_3E polyhedra with increasing M_yO_z (M=Ga, Sb and W) content.

2-The antimony atoms present mixed oxidation state (Sb^{3+}, Sb^{5+}) involving coexistence of several coordination polyhedra.

3-The tungsten atoms are always located in distorted WO_6 octahedra : the distortion increases with WO_3 content.

4-Whatever the composition, gallium atoms present mixed environment GaO_4 and GaO_6.

Nonlinear measurements on these glass materials were performed. The highest nonlinear susceptibilities χ^3 values are obtained for TeO_2-WO_3 glasses having transition ion with empty d orbitals.

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