

Comparative structural investigation of B₂O₃-MO-CuO glasses (MO → TeO₂ or As₂O₃) by FTIR and Raman spectroscopies

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Glasses of the systems xCuO·(100-x)[2B₂O₃·MO] with MO → TeO₂ or As₂O₃ and 0 ≤ x ≤ 30 mol % were prepared and investigated by FTIR and Raman spectroscopies. These methods were used, knowing the fact that they allowed to distinguish the local structural units, which on the whole, are in charge for the glasses structure and give their physical properties. The results were comparatively analyzed having in view the valence states of the glass matrix modifiers cations (Te⁴⁺ or As³⁺). It was evidenced that the network structure of the studied glasses is mainly based on the BO₃ and BO₄ units, the BO₃ units being dominant. The influence of both, nature of the vitreous network modifiers and copper content (x), on the N_{BO4}/N_{BO3} ratio evolution was evidenced.

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1. Introduction

B₂O₃-based glasses have been widely studied over the years due their interesting structural particularities as the occurrence of boron anomaly [1, 2]. Being good shield against infrared radiation, the borate glasses are often used as dielectric and insulating materials. Due their optical properties such, high refractive index and high optical nonlinearity, the B₂O₃-TeO₂ glasses are also of interest for various optical devices [3-5]. The studies made on this glass categories have shown the progressively changes of boron and tellurium coordination with the other ions addition. The change of boron coordination from three to four along with the formation of BO₄ tetrahedra and also several other structural groups were observed. Moreover, the conversion of trigonal bipyramids TeO₄ (tbp) in TeO₃ trigonal pyramids (tp) along with the formation of non bridging oxygen atoms was also found [6-8].

As₂O₃ is a strong network former with corner-sharing AsO₃ pyramidal units; when As₂O₃ is present in B₂O₃ glass network, it is quite likely for a cross linking of a part of BO₃ units with AsO₃ units to form B-O-As bonds in the glass network. So that, is expected that the infrared transmission and the Raman scattering of borate glasses to be affected by the As₂O₃ addition [9].

This paper presents our results concerning the structural modifications of two glass systems CuO-B₂O₃-TeO₂ and CuO-B₂O₃-As₂O₃. These systems were investigated by two very powerful complementary methods in elucidating the glasses structure, the FTIR and Raman spectroscopies.

2. Experiment

Two series of samples from xCuO·(100-x)[2B₂O₃·MO] with MO → TeO₂ or As₂O₃ systems were prepared using pure reagent grade compounds, *i.e.* H₃BO₃, TeO₂, As₂O₃ and CuO in appropriate ratios. The mixtures corresponding to the desired compositions were melted in air, in sintered

corundum crucibles, and in an electric furnace at 1250 °C (t = 30'). The melts were quenched at room temperature by pouring onto stainless steel plates.

The structure of the samples was tested by means of X-ray diffraction and no crystalline phase was detected up to 30 mol % CuO. The FT-IR absorption spectra were recorded with an Equinox 55 Bruker spectrometer using the KBr pellet technique. The FT-Raman spectra have been recorded for bulk glasses using an integrated FRA 106 Raman module in a 180° scattering geometry, at room temperature, using for excitation the 1064 nm line of Nd-YAG laser with an output power of 500 mW. The spectral resolution was 1 cm⁻¹.

3. Results and discussion

The experimental FT-IR spectra for the xCuO·(100-x)[2B₂O₃·MO] with MO → TeO₂ or As₂O₃ and 0 ≤ x ≤ 30 mol % are presented in Figs. 1a and 1b. The absorption bands detected in the FT-IR spectra of these two series of glasses and their assignments are summarized in Tables 1 and 2. The results have been discussed on the basis of the method given by Condrad and Tarte [10, 11] by comparing the experimental data of glasses with those of related crystalline compounds. The characteristic absorption bands for the vitreous B₂O₃, TeO₂ and As₂O₃ [6, 12-18] and crystalline CuO [12] were used as a reference point in the results discussion. We propose a structure mainly built by tri- (B₃O₅⁻), tetra- (B₈O₁₃²⁻), penta- (B₅O₈⁻), pyro- (B₂O₇⁴⁻), ortho-borate (BO₃³⁻) and diborate groups (B₄O₇²⁻) groups for both glass systems investigated (Ø: oxygen atom bridging two boron atoms and O⁻: nonbridging oxygen atom) [6, 12-16]. Moreover, TeO₄ tbp and TeO₃ tp [7, 8, 17, 18] were detected in structure of borate-telluride glasses while As-O bond vibrations from arsenic trioxide [12, 19] were evidenced in borate-arsenite based glasses.

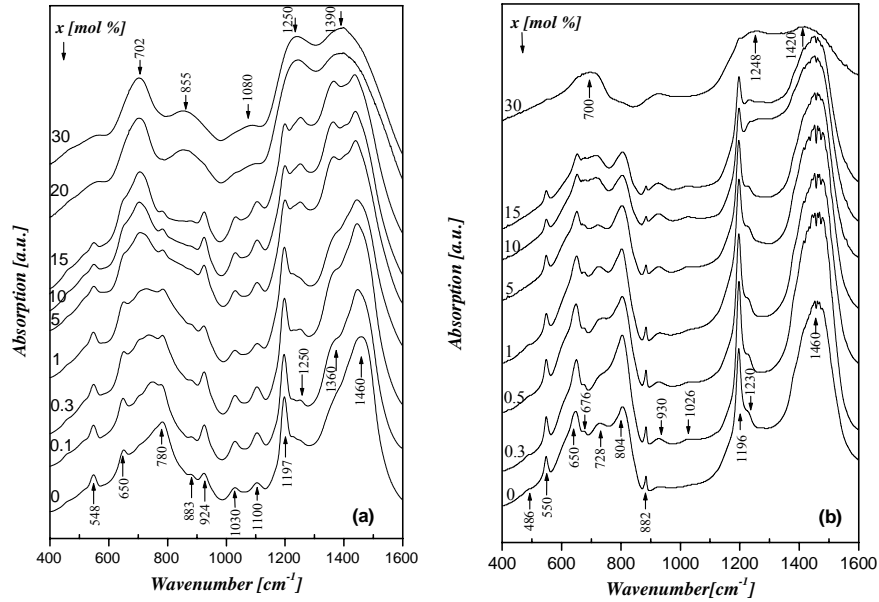


Fig. 1. FT-IR spectra of $x\text{CuO} \cdot (100-x)[2\text{B}_2\text{O}_3 \cdot \text{TeO}_2]$ (a) and $x\text{CuO} \cdot (100-x)[2\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ (b) glasses.

Table 1. * Frequencies and their assignments for FT-IR and Raman spectra of $x\text{CuO} \cdot (100-x)[2\text{B}_2\text{O}_3 \cdot \text{TeO}_2]$ glass system.

Wavenumber [cm ⁻¹]		IR assignments	Raman assignments
IR	Raman		
	~320		TeO ₃ tp units with two or three nonbridging oxygen
	~430		bending and stretching vibration of Te-O-Te linkages
~548	~540	B-O-B bonds bending vibration	isolated diborate groups
~650	~660	O-B-O bonds bending vibration Te-O bonds stretching vibration in TeO ₄ units	stretching vibration of TeO ₄ tbp units and TeO ₃₊₁ polyhedra
~700		O ₃ B-O-BO ₃ bonds bending vibration Te-O bonds stretching vibration in TeO ₃ units	
~780	~760	O ₃ B-O-BO ₄ bonds bending vibration	TeO ₄ tbp, stretching vibration of Te-O from TeO ₃ tp units or TeO ₃₊₁ polyhedra and symmetric breathing vibration of six member ring with a BO ₃ triangle replaced by a BO ₄ tetrahedra
	~804		symmetric breathing vibration of boroxol rings
~883 ~1030	~860	B-O bonds stretching vibration of BO ₄ ⁻ ; tetrahedra from tri-, tetra- and penta-borate groups	Te-O-B mode
~925	~920	B-O bonds stretching vibration in BO ₄ units from diborate groups	orthoborate triangles
~1100		asymmetric stretching vibration of B-O bonds from BO ₄ units	
~1196		asymmetric stretching vibration of B-O and / or B-O' bonds in borate triangular units (BO ₃ and BO ₂ O') from pyro- and orthoborate groups	
~1250		asymmetric stretching vibration of B-O bonds from orthoborate groups	
~1360 ~1460		B-O bonds stretching vibration of BO ₃ units from various borate groups	

* for details and references see text.

Table 2. * Frequencies and theirs assignments for FT-IR and Raman spectra of $x\text{CuO} \cdot (100-x)[2\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glass system.

Wavenumber [cm^{-1}]		IR assignments	Raman assignments
IR	Raman		
~550	~500	B-O-B bonds bending vibration	As-O bonds vibration
~650		O-B-O bonds bending vibration	
~676	~690	B-O-B bonds bending vibration from pentaborate groups	chain and/or ring type metaborate groups
~728	~780	$\text{O}_3\text{B-O-BO}_3$ bonds bending vibration	symmetric breathing vibration of six member ring with a BO_3 triangle replaced by a BO_4^- tetrahedra (tri-, tetra- and pentaborate groups)
~804	~806	As-O bonds vibration	symmetric breathing vibration of boroxol rings
~882 ~1026		B-O bonds stretching vibration of BO_4 tetrahedra from tri-, tetra- and pentaborate groups	
~930	~975	B-O bonds stretching vibration in BO_4 units from diborate groups	orthoborate triangles
~1196		asymmetric stretching vibration of B-O and / or B-O ⁻ bonds in borate triangular units (BO_3 and BO_2O^-) from pyro- and orthoborate groups	
~1230		asymmetric stretching vibration of B-O bonds from orthoborate groups	
~1460	~1350	B-O bonds stretching vibration of BO_3 units from various borate groups	pyroborate groups

* for details and references, see text.

We chose to discuss the structural changes involved by the CuO content addition on the bases of $A_r = A_4/A_3$ ratio (A_4 and A_3 were calculated as the integral of the absorption signal in the $800\text{-}1150\text{ cm}^{-1}$ (A_4) and $1150\text{-}1550\text{ cm}^{-1}$ (A_3) spectral ranges) [6]. The A_4 and A_3 reflect the relative content of tetrahedral (BO_4^-) and triangular (BO_3 and BO_2O^-) borate species respectively. The A_r ratio versus CuO content is given in Fig. 2 where the dotted lines is just a guide for the eyes. For all the investigated glasses the A_r values are lower than 1, showing the predominance of BO_3 units in these glasses structures. The ascending trend of the A_r ratio in the first part of the compositional range ($x \leq 10$ mol %) indicates a progressively changes of boron coordination from three to four. In both series of glasses, for $x > 10$ mol %, a descendent behaviour was observed for A_r values with the copper addition proving the structures depolymerization tendency along with the nonbridging oxygen atoms numbers increasing.

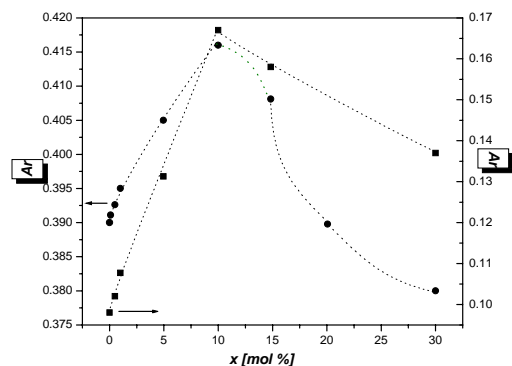


Fig. 2. A_r ratio evolution with the x values for $x\text{CuO} \cdot (100-x)[2\text{B}_2\text{O}_3 \cdot \text{TeO}_2]$ (●) and $x\text{CuO} \cdot (100-x)[2\text{B}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ (■) glasses.

For borate-telluride glasses the copper addition implies the conversion of TeO_4 tbp into TeO_3 tp along with the formation of non bridging oxygen atoms. These structural changes are evidenced by the ascending trend of the absorption bands centered at $\sim 700\text{ cm}^{-1}$ concomitantly with the decreasing of the $\sim 650\text{ cm}^{-1}$ absorption band intensity. In case of borate-arsenite glasses, the As-O detected bonds tend to be destroyed with the copper addition.

For both glass systems, the copper addition implies a decreasing of FT-IR absorption bands number and their

intensity showing a progressively disordering (depolymerization) of a vitreous networks with the CuO addition (CuO acting as a vitreous network modifier) and increasing of the infrared transmittance properties of these glasses.

As it can be seen from Fig. 2, the Ar values are higher in case of CuO-2B₂O₃-TeO₂ glasses than that of CuO-2B₂O₃-As₂O₃ one, revealing a higher degree of polymerization for glasses with tellurium.

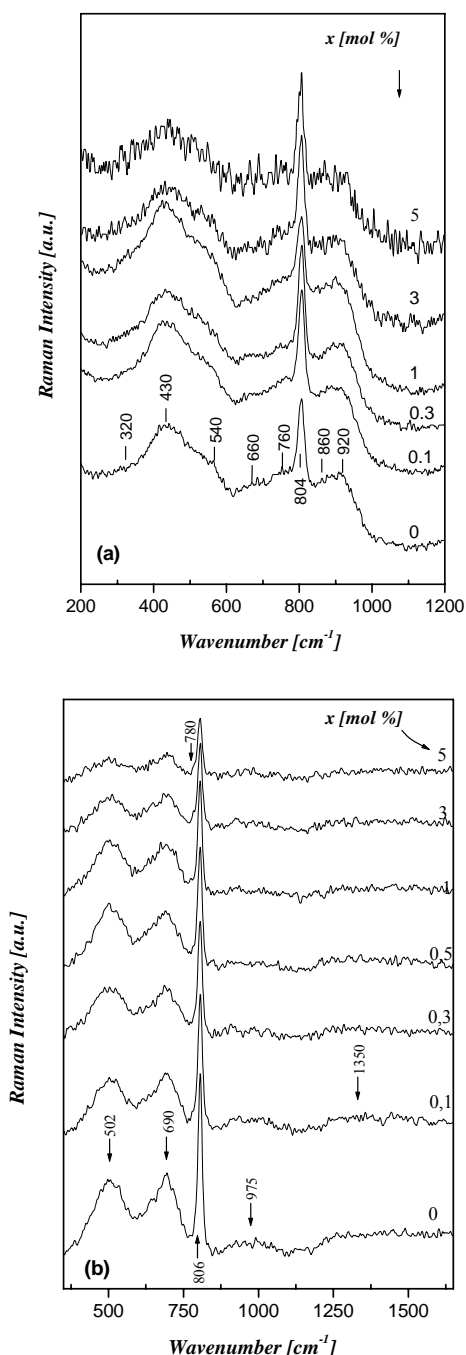


Fig. 3. Raman spectra of $x\text{CuO}\cdot(100-x)[2\text{B}_2\text{O}_3\cdot\text{TeO}_2]$ (a) and $x\text{CuO}\cdot(100-x)[2\text{B}_2\text{O}_3\cdot\text{As}_2\text{O}_3]$ (b) glasses.

The noisy Raman spectra were recorded for these two series of glasses in the 0-5 mol % compositional range (Figs. 3a and 3b). The detected Raman scattering bands and their assignments are shown in Tables 1 and 2 for both glass systems. As it can be seen for the Raman bands assignments, the obtained data confirm for both analyzed glass systems the structures proposed by the FT-IR results and their evolution with the copper addition. Additional, new structural groups were detected boroxol ring (B₃O_{4.5}) in the glass structures of both series and chain and/or ring type metaborate groups [6,13,14] in borate-arsenite glasses. For all the investigated Raman samples the $\sim 805\text{ cm}^{-1}$ line assigned to the boroxol ring is predominant.

The $\sim 805\text{ cm}^{-1}$ band intensity had different behaviour with the copper addition for these two analysed glass systems: increases in case of CuO-2B₂O₃-TeO₂ glasses and decreases for CuO-2B₂O₃-As₂O₃ glasses. This behavior come to support the FT-IR results relating to the higher degree of polymerization for glasses containing tellurium reported to those containing arsenic.

4. Conclusions

Two homogeneous series of glasses, $x\text{CuO}\cdot(100-x)[2\text{B}_2\text{O}_3\cdot\text{MO}]$ with MO → TeO₂ or As₂O₃, were obtained within $0 \leq x \leq 30$ mol %. The FT-IR and Raman spectra of these glasses have been analyzed in order to identify its local structural peculiarities. The influence of both glass matrix composition and copper ions addition on the glasses network was analysed.

The infrared data revealed the presence of boron atoms in coordination states, three and four, for all investigated glasses. The tetra coordinated boron atoms number is lower than that three coordinated for all samples. Higher values of BO₄/BO₃ ratio were found in case of system that contains tellurium revealing a higher degree of polymerization of these glasses comparatively with those that contain arsenic. The boron atoms are placed in the same structural groups in both glass systems. Additional TeO₄ tpb and TeO₃ tp and vibrations of As-O bond were detected in glasses tellurium and respectively arsenic. For a same x value, the change of the glass matrix composition from 2B₂O₃-TeO₂ to 2B₂O₃-As₂O₃ implies a decreasing of the glasses networks polymerization degree.

Raman data confirm the structure proposed by the FT-IR spectroscopy and more over detect new structural groups, i.e. boroxol ring for both series of investigated glasses and chain and/or ring type metaborate groups for borate-arsenite samples. Both spectroscopic methods revealed the copper ions modifier role, the recorded spectra changing continuously at those additions.

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