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Structural investigation of $CuO-Bi_2O_3-B_2O_3$ glasses by FT-IR, Raman and UV-VIS spectroscopies

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Glasses from $xCuO\cdot(100-x)[2Bi_2O_3\cdot B_2O_3]$ system were studied by means of FT-IR, Raman and UV-VIS spectroscopies in order to obtain informations about the changes that appear in the structure of $2Bi_2O_3\cdot B_2O_3$ glass matrix with the doping of copper ions. FT-IR measurements indicate that the network structure of the studied glasses is based on the BiO_3 pyramidal and BiO_6 octahedral units and also on BO_3 and BO_4 units. The Raman spectra evidenced the presence of the structural units established by IR absorption and also of some other characteristic structural units. The FT-IR and Raman spectra do not present any absorption bands characteristic to CuO, but the absorption of Bi_2O_3 and B_2O_3 structural units depends of its presence in the glass matrix. The UV-VIS absorption spectra for all glasses have a single asymmetric band, which corresponds to a $^2B_{1g}\rightarrow {}^2B_{2g}$ transition of the Cu^{2+} ions in octahedral symmetry with an elongated tetragonal distortion. These measurements indicate the presence of Cu^{2+} ions in the glasses.

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1. Introduction

Bismuthate oxide glasses have been extensively investigated following the pioneering papers of Dumbaugh [1, 2]. Interest for these glasses has increased for their optical properties [3, 4] and ability to synthesize high – temperature ceramic – superconductors [4]. The structure of bismuthate oxide glasses has been studied by IR [5, 6], Raman [5, 7] and EXAFS [8] spectroscopic methods. In all the binary and multicomponent bismuthate glasses were identified two structural units: pyramidal BiO_3 and octahedral BiO_6 units in variable proportion [5-8]. B_2O_3 is one of the most common glass former and is present in almost all important commercially glasses. The borate glasses are used as dielectric materials and good shielding material of IR radiation. They are also of academic interest due to the occurrence of the boron anomaly [9]. The structure of the B_2O_3 glass was investigated by X-ray [10] and neutron [11] diffraction, IR [12], Raman [12, 13] and NMR [14] spectroscopies. All studies report that B_2O_3 is composed essentially of BO_3 triangles forming boroxol rings. Moreover, the addition of modifier oxides to B_2O_3 changes some BO_3 triangles to BO_4 tetrahedron, which exists in different structural borate groups [12-14].

The introduction of transition-metal oxide in the glass matrix changes the structure of glasses, where the metal oxide is acting as a modifier and can determine semiconducting properties of the glasses [15].

This paper present our results regarding the structure of $xCuO\cdot(100-x)[2Bi_2O_3\cdot B_2O_3]$ glass system obtained by FT-IR, Raman and UV-VIS spectroscopies.

2. Experimental

Glasses of $xCuO\cdot(100-x)[2Bi_2O_3\cdot B_2O_3]$ system were prepared using reagent grade purity H_3BO_3, $Bi(NO_3)_3\cdot 5H_2O$ and CuO in suitable proportion to obtain the desired compositions. According to upper formula, the compositions were mixed and introduced directly in an electric furnace at 1250 ^oC for 5 minutes. Sintered corundum crucibles were used. The structure of the samples was studied by means of X-ray diffraction and no crystalline phase was detected up to 50 mol % CuO.

The infrared absorption spectra were recorded using Equinox 55 Bruker spectrometer in the range of 400 – 1400 cm^{-1}. The measurements were performed using the KBr pellet technique. The Raman spectra have been recorded using LabRam spectrometer. The spectra were collected in the back-scattering geometry and the detection of Raman signal was carried out with a Photometric model 9000 CCD camera. The UV-VIS absorption spectra were recorded with Lamnda19 spectrometer in the wavelength region 550 – 1100 nm. All the measurements were recorded at room temperature.

3. Results and discussion

3.1. Infrared data

The FT–IR spectra of $xCuO\cdot(100-x)[2Bi_2O_3\cdot B_2O_3]$ glass system, with $0 \le x \le 50$ % mol are presented in Fig. 1 and the assignments of the detected absorption band are summarized in Table 1. These data have been discussed on the basis of the method given by Tarte [16] and Condrate [17] by comparing the experimental data of glasses with those of related crystalline compounds. In this paper the characteristically absorption bands for the crystalline CuO [18], vitreous B_2O_3 [19, 20] and Bi_2O_3 [6, 21] were used.

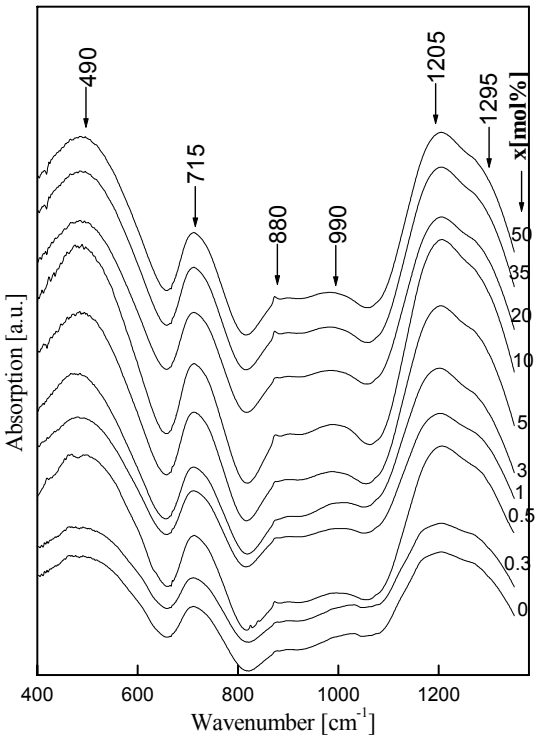

Fig. 1. FT – IR spectra of $xCuO\cdot(100-x)[2Bi_2O_3\cdot B_2O_3]$ glass system.

The FT – IR spectra of the crystalline α - Bi_2O_3 presents six absorption bands at: ~ 380 cm^{-1}, ~ 425 cm^{-1}, ~ 465 cm^{-1}, ~ 510 cm^{-1}, ~ 540 cm^{-1} and ~ 595 cm^{-1}, characteristic to the vibrations of Bi-O bonds in BiO_6 polyhedra [6, 21]. For the Bi_2O_3, in FT – IR spectra, were identified five absorption bands at: ~ 350 cm^{-1}, ~ 470 cm^{-1}, ~ 540, ~ 620 cm^{-1} and ~ 840 cm^{-1}, characteristic to the vibrations of Bi-O bonds in BiO_3 units [6, 21].

The characteristic FT – IR absorption bands for vitreous B_2O_3 were identified at ~ 720 cm^{-1}, ~ 1260 cm^{-1} and ~ 1420 cm^{-1}, which are attributed to the B-O bonds vibrations in BO_3 units [22]. The vibrational modes of the borate glasses network show the presence of three infrared spectral regions [23]. The first group of bands, which occur at 1200 – 1600 cm^{-1}, is due to the asymmetric stretching relaxation of the B – O bonds of trigonal BO_3 units, the second group lies between 800 and 1200 cm^{-1} and is due to the B – O bonds stretching of the tetrahedral BO_4 units and the third groups is observed around 700 cm^{-1} and is due to bending of B – O – B linkages in the borate network.

Table 1. Frequencies and their assignments for FT-IR and Raman absorption bands of $xCuO\cdot(100-x)[2Bi_2O_3\cdot B_2O_3]$ glasses.

Wavenumber (cm^{-1})		**FT – IR assignment**	**Raman assignment**
FT - IR	**Raman**		
	~ 235		Bi-O bonds vibrations in BiO_3 and BiO_6 units
	~ 315		Bi-O-Bi stretching vibrations in distorted BiO_6 units
~ 490		Stretching vibrations of Bi-O bonds in strongly distorted BiO_6 units, B-O-B bonds bending vibrations	
	~ 585		$Bi-O^-$ stretching vibrations in BiO_6 units, Vibrations of ring type metaborate groups
~715	~ 724	Symmetric stretching vibrations of Bi-O bonds in BiO_3 units, O_3B-O-BO_3 bending vibrations	Vibrations of chain type metaborate groups
	~ 824		Vibrations of pyroborate groups
~880		Symmetric stretching vibrations of Bi-O bonds in the BO_3 units, Stretching vibrations of B-O bonds in BO_4 units from diborate groups	
~ 990	~ 950	Stretching vibrations of B-∅ bonds in $B∅_4$ units from tri-, tetra- and penta-borate groups	Vibrations of orthoborate groups
~1205	~ 1205	Stretching vibrations of B-O bonds in BO_3 units from meta- and ortho -borate groups	Symmetric stretching vibrations of terminal $B-O^-$ bonds in pyroborate groups
~1295		Asymmetric stretching vibrations of B-O bonds in BO_3 and $B∅_2O^-$ units	
	~ 1330 ~ 1584		$B-O^-$ bonds stretching vibrations involving nonbridging oxygen (NBO) in various borate groups

∅ - oxygen atom bridging two boron atoms

In the FT – IR spectrum of the studied glass matrix are present six well-defined bands at ~ 490 cm^{-1}, ~ 715 cm^{-1}, ~ 880 cm^{-1}, ~ 990 cm^{-1}, ~ 1205 cm^{-1} and ~ 1295 cm^{-1}. The absorption band at ~ 490 cm^{-1} is assigned to the stretching vibrations of Bi – O bonds in strongly distorted BiO_6 units [6, 21] over witch can be superposed the B – O – B bonds bending vibrations [22]. The intensity of this band is increasing up to x = 10 mol % and after decrease. The band from ~ 715 cm^{-1} is assigned to the symmetric stretching vibrations of Bi – O bonds in BiO_3 units [24] over which can be superposed the O_3B – O – BO_3 bending vibrations [20, 23]. The intensity of this band increase up to x = 10 mol % and for samples with x ≥ 20 mol % remain the same with the increasing of the copper content. The absorption band from ~ 880 cm^{-1} is assumed to be due to the symmetric stretching vibrations of Bi – O bonds in BiO_3 units [6] on which can be superposed the stretching vibrations of B – O bonds in BO_4 units from diborate groups [20]. For samples with x ≥ 0.3 mol % the intensity of this bands increases slowly with the increasing of the copper content. The presence of the B – O stretching vibrations in BO_4 units in tri-($B_3O_5^-$), tetra- ($B_8O_{13}^{2-}$) and penta-($B_5O_8^-$) - borate groups is attested by FT-IR absorption band from ~ 990 cm^{-1} [20]. This band is increasing up to x = 10 mol % and then remains the same. The strong band at ~ 1205 cm^{-1} is assigned to stretching vibrations of B – O bonds in BO_3 units from meta- and orto- borate groups [23, 25]. The intensity of this band is maximum for x = 10 mol % and for higher concentration of the copper ions remains approximately the same. The appearance of the vibrational shoulder at ~ 1295 cm^{-1} for all the studied glasses is assigned to asymmetric stretching vibrations of B – O bonds in BO_3 units [23, 26]. The amplitude of this band remains the same for all the compositional range.

It must remark that the band corresponding to the FT – IR absorption of CuO was not evidenced even for glasses with high concentration of copper. The copper addition in the glasses affected a little, as it can be see from figure 1, the intensity of the absorption bands in the manner that depends of these bands. These data evidenced that the formed structure of $2Bi_2O_3 \cdot B_2O_3$ glass matrix is very stable and is not influenced by the doping with copper ions.

The presence of two network formers in these glasses made to obtained FT-IR spectra to resume of some overlapping of certain absorption bands given by different Bi – O and B – O linkage vibrations (Table 1). This fact made difficult the prediction of certain structure for these glasses. However, the bismuth ions placed in BiO_3 pyramids and BiO_6 distorted octahedron, which were detected from its characteristic Bi-O bonds infrared vibration, also the boron ions are placed in BO_3 (infrared absorption present in the range 1100- 1400cm^{-1}) and BO_4 (infrared absorption present in the range 800-1100 cm^{-1}) units from various borate groups. The dominant infrared absorption of these glasses is due to the Bi – O bonds vibrations in BiO_6 (centered at ~ 490 cm^{-1}) and BiO_3 (centered at ~ 715 cm^{-1}) units and those of B – O bonds vibrations in BO_3 units (present in range ~ 1205 cm^{-1} and ~ 1295 cm^{-1})) , the BO_4/BO_3 ratio being sub unit.

3.2. Raman data

The Raman spectra of $xCuO \cdot (100\text{-}x)[2Bi_2O_3 \cdot B_2O_3]$ glass system, with 0 ≤ x ≤ 35 mol % are presented in Fig. 2 and the assignments of the detected absorption bands are summarized in Table 1. In the glass matrix spectrum the following bands are present: ~ 235 cm^{-1}, ~ 315 cm^{-1}, ~ 585 cm^{-1}, ~ 724 cm^{-1}, ~ 950 cm^{-1}, ~ 1205 cm^{-1}, ~ 1330 cm^{-1} and ~ 1584 cm^{-1}.

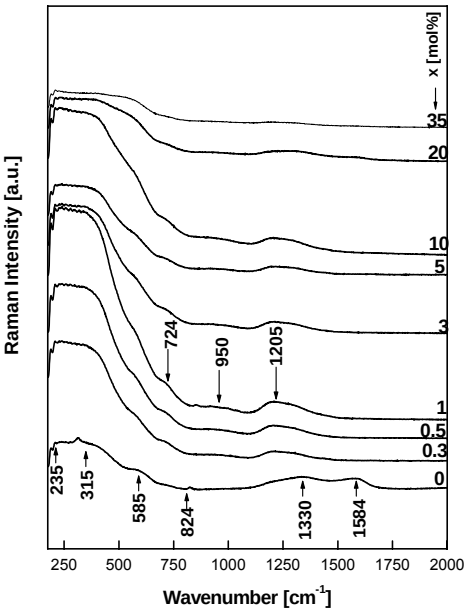

Fig. 2. Raman spectra of $xCuO \cdot (100\text{-}x)[2Bi_2O_3 \cdot B_2O_3]$ glass system.

The band from ~ 235 cm^{-1} indicates the presences in the glass matrix of the Bi – O vibrations in BiO_3 and BiO_6 units [27]. This band is increasing gradual with the increasing of copper concentration and for samples with x > 10 mol % then decreases. The bands from ~ 315 cm^{-1} is assigned to Bi – O – Bi stretching vibrations in distorted BiO_6 octahedral units [27]. This band is increasing for samples up to x = 1 % mol then for higher concentration decreases gradual with the increasing of the copper concentration until x = 35 mol % where it cannot be observed. It can be observed for all the samples a weak band centered at ~ 585 cm^{-1}, which can be attributed to both vibrations, of the Bi – O – Bi in distorted BiO_6 polihedra [27] and vibrations of ring type metaborate groups [20, 28-30], The addition of copper ions in the glass matrix involves an increasing in the intensity of this band up to x = 1 mol % and after decrease. In the samples with x > 0 mol % can be observed the apparition of a weak band centred at ~ 724 cm^{-1} which is characteristic to vibrations of chain type metaborate groups [28-32]. The intensity of this band increases until 1 mol% and for samples with x = 35 % mol disappears. The band centered at ~ 824 cm^{-1} appears for the samples with 0 ≤ x ≤ 1 mol

% and is assigned to vibrations of pyroborate groups [20, 28-30]. For samples with x ≥ 3 mol % this band disappears. The band centered at ~ 950 cm^{-1} appears for the samples with x > 0 mol % and is assigned to vibrations of orthoborate groups [28-30]. The intensity of this band is maximum for sample with x = 1 mol % and for samples with x = 20 mol % disappears. At ~ 1205 cm^{-1}, for the samples with x > 0 mol %, the spectra present a band assigned to the symmetric stretching vibrations of terminal B – O^- bonds in pyroborate groups [32]. The bands centered at ~ 1330 cm^{-1} and ~ 1584 cm^{-1} respectively, characteristic only to the glass matrix, are corresponding to the B – O^- stretching vibrations in various borate groups [20, 33, 34]. By doping of the copper in the glass matrix leads to the breaking of B – O^- bonds from various borate groups.

The Raman absorption spectra evidence that the bismuth ions are incorporated in the glass network as BiO_3 and BiO_6 polyhedra and the boron ions are incorporated in various borate groups. The presence of these structural units in the glass structure depends on the copper content, but the presence of CuO was not evidenced in the Raman spectra. From the shape of Raman spectra results that the glasses become more disordered for x ≥ 35 mol%.

3.3. Optical absorption

The UV-VIS absorption spectrum of Cu^{2+} ions in $[2Bi_2O_3 \cdot B_2O_3]$ glass matrix observed at room temperature have been recorded in the wavelength region 550 – 1100 nm and are shown in Fig. 3. Free Cu^{2+} ion has a $3d^9$ configuration, which splits under an octahedral crystalline field to give degenerate e_g orbitals as the lowest ($|x^2-y^2>$, $|3z^2-r^2>$) and degenerate t_{2g} orbitals ($|xy>$, $|yz>$, $|zx>$) the higher in energy. Tetragonal crystalline field lifts some of the degeneracy leaving either ($|x^2-y^2>$) or ($|3z^2-r^2>$) as the lowest.

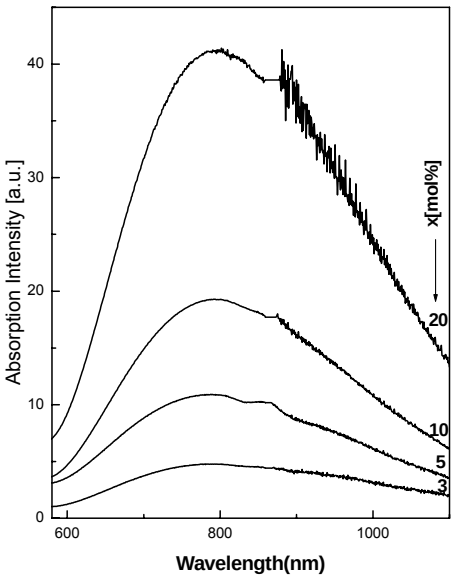

Fig. 3. Optical absorption spectra of xCuO·(100-x)[2Bi2O3·B2O3] glass systems.

This band observed for all the samples from $xCuO \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$are similar, showing one strong band centered at 800nm, corresponding to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition [35, 36]. The intensity of this band increases with increasing the copper concentration. This broad band can be identified as the d-d transitions due to Cu^{2+} ions and described in terms of the ligand field theory [35]. Karthikeyan et all [36] reported similar observations for the optical studies of Cu^{2+} doped sodium borobismuthate glasses.

4. Conclusion

Homogeneous glasses of the xCuO·(100-x)$[2Bi_2O_3 \cdot B_2O_3]$ system were obtained within 0 ≤ x ≤ 50 mol %. FT – IR and Raman spectra of these glasses have been analysed to identify the spectral contribution of each component on the structure and to point out the role of the copper ions as a modifier of the glass network. The FT – IR studies indicates the presences in structure of the studied glasses of BiO_3, BiO_6, BO_3 and BO_4 units, but their proportion depends on the presence of copper ions in these glasses. Raman studies complete the structure established by FT – IR spectroscopy indicating also the presence of other structural units in the studied glasses. From the shape of Raman spectra results that for x ≥ 35 mol%, the structure of the studied glasses become more disordered.

The presence of CuO was not directly evidenced by FT – IR and Raman measurements, but the UV – VIS absorption certifies the presence of Cu^{2+} in the glass network. The additon of copper ions in the glasses determine the increasing of the intensity of the optical absorption band of xCuO·(100-x)$[2Bi_2O_3 \cdot B_2O_3]$ glasses.

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