

FT-IR and Raman investigations of MnO-B₂O₃-Bi₂O₃ glasses

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The influence of manganese ions content on the structure of 2Bi₂O₃·B₂O₃ glass matrix was investigated by means of FT-IR and Raman spectroscopies. Experimental FT-IR data reveal that the structure of 2Bi₂O₃·B₂O₃ glass is based on the BiO₆ octahedral and BiO₃ pyramidal and also on BO₃ and BO₄ units. The Raman spectra confirm the presence in glass matrix of the structural units established by FT-IR absorption and also evidenced some other structural units characteristic for this glass network. The FT-IR and Raman spectra of the studied glasses does not evidence directly absorption bands specific to the MnO, but the absorption bands characteristic for the glass matrix are influenced by the presence of the manganese ions in this glass structure.

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1. Introduction

FT-IR and Raman spectroscopies have been proved to be powerful and effective tools for characterize the local structure of the oxide glasses.

Interest in bismuthate oxide glasses has increased due to their interesting physical properties [1-4] 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 these studies has been evidenced that the binary and multicomponent bismuthate glasses are containing two types of structural units: pyramidal BiO₃ and octahedral BiO₆ units in variable proportion [5-8].

B₂O₃ is one of the most common glass formers and is present in almost all commercially glasses. Simultaneously with technical applications, the borate glasses have also academic interest due to the occurrence of the boron anomaly [9]. The structure of the B₂O₃ glass was investigated by X-ray [10] and neutron [11] diffraction, IR [12], Raman [12, 13] and NMR [14] spectroscopies. These studies indicate that the B₂O₃ glass is composed essentially from BO₃ triangles forming boroxol rings. At the same time, the addition of modifier oxides to B₂O₃ changes some BO₃ triangles to BO₄ tetrahedron, which exists in different structural borate groups [12-14].

The introduction of transition metal ions (TMI) in the oxide glass matrices changes the structure of the glass network, were TMI can act as a modifier and can determine semiconducting behavior of the glasses [15].

In this paper we present our data regarding to the structural changes in 2Bi₂O₃·B₂O₃ glass matrix determined by controlled doping with MnO, using FT-IR and Raman spectroscopies.

2. Experimental

Glasses of xMnO·(100-x)[2Bi₂O₃·B₂O₃] system were prepared using reagent grade purity H₃BO₃, Bi(NO₃)₃·5H₂O and MnCO₃ in suitable proportion to obtain the desired compositions. According to upper formula, the starting materials were mixed and introduced directly in an electrical furnace at 1250^o C 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 % MnO.

The infrared absorption spectra were recorded using Equinox 55 Bruker spectrometer in the range of 400 – 1600 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. All the measurements were recorded at room temperature.

3. Results and discussion

3.1. Infrared data

The experimental FT-IR spectra of xMnO·(100-x)[2Bi₂O₃·B₂O₃] glass system, with 0 ≤ x ≤ 50 mol % are presented in figure 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 obtained for the studied glasses with those of related crystalline compounds. In this paper the characteristically absorption bands for the crystalline

MnO₂, Mn₃O₄ [18], Bi₂O₃ [6, 19] and vitreous B₂O₃ [20-22] were used.

The FT-IR spectra of the crystalline α -Bi₂O₃ 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 BiO₆ octahedral units [6, 19]. For the Bi₂O₃, in FT-IR spectra, were identified five absorption bands at: ~ 350 cm⁻¹, ~ 470 cm⁻¹, ~ 540 cm⁻¹, ~ 620 cm⁻¹ and ~ 840 cm⁻¹ characteristic to the vibrations of Bi-O bonds in BiO₃ pyramidal units [6, 19]. The characteristic FT-IR absorption bands for vitreous B₂O₃ were identified at ~ 720 cm⁻¹, ~ 1260 cm⁻¹ and ~ 1420 cm⁻¹, which are attributed to the B-O bonds vibrations in BO₃ units [20-22]. 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 in BO₃ units, the second group lies between 800 and 1200 cm⁻¹ and is due to the B-O bonds stretching in BO₄ units and the third group is observed around 700 cm⁻¹ and is due to bending of B-O-B linkages in the borate network. The characteristic absorption bands for the crystalline MnO₂ were identified at ~ 335 cm⁻¹, ~ 400 cm⁻¹ and ~ 615 cm⁻¹ and for Mn₃O₄ were identified at ~ 393 cm⁻¹, ~ 475 cm⁻¹ and ~ 600 cm⁻¹ [18].

The FT-IR spectra of the studied glass matrix (2Bi₂O₃·B₂O₃) presents the following absorption bands at ~ 480 cm⁻¹, ~ 540 cm⁻¹, ~ 720 cm⁻¹, ~ 873 cm⁻¹, ~ 1030 cm⁻¹, ~ 1190 cm⁻¹ and ~ 1340 cm⁻¹.

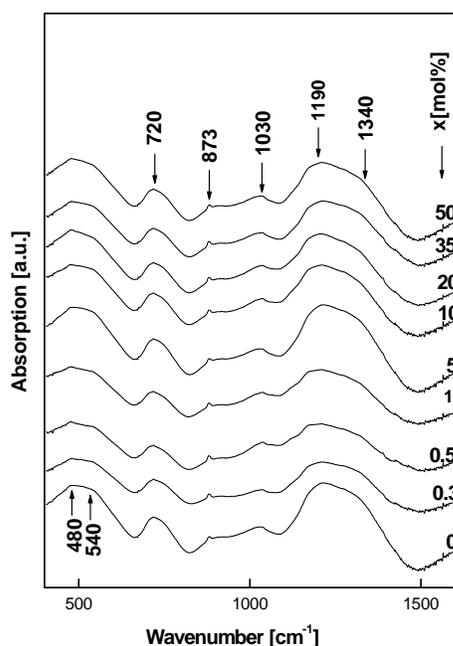


Fig.1. FT-IR spectra of $x\text{MnO}\cdot(100-x)[2\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3]$ glasses.

The bands centered at ~ 480 cm⁻¹ and ~ 540 cm⁻¹ are assigned to the stretching vibrations of Bi-O bonds in strongly distorted BiO₆ units [6, 19]. Over the first band the B-O-B bonds bending vibrations [22] and the contribution of specific vibrations of Mn-O bonds [18] can be superposed. The addition of MnO to the glass matrix determines the decreasing of intensity of these bands up to $x = 1$ mol % and increasing for samples with $x \geq 1$ mol %.

The band from ~ 720 cm⁻¹ is assigned to the symmetric stretching vibrations of Bi-O bonds in BiO₃ units [24] over which can be superposed the O₃B-O-BO₃ bending vibrations [21, 23]. For samples with $x \leq 1$ mol % the intensity of this band decreases and for higher MnO content the intensity slowly increases.

The absorption band centered at ~ 873 cm⁻¹ is assigned to the symmetric stretching vibrations of Bi-O bonds in BiO₃ units [6] on which can be superposed the stretching vibrations of B-O bonds in BO₄ units from diborate groups [21]. The intensity of this band remains approximately the same in all concentration range.

The band from ~ 1030 cm⁻¹ is assumed to be due to the B-O stretching vibrations in BØ₄ units from tri-, tetra- and penta-borate groups (Ø oxygen atoms bridging two boron atoms) [21]. The amplitude of this band is slowly decreasing up to $x = 0.3$ mol % and after increases, and remains the same for $x \geq 5$ mol %. So, the addition of manganese ions in 2Bi₂O₃·B₂O₃ glass matrix determines the little influence on the proportion of tetracoordinated boron ions.

The dominant band in the FT-IR spectra of $x\text{MnO}\cdot(100-x)[2\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3]$ glass system is at ~ 1190 cm⁻¹. This band was assigned to the stretching vibrations of B-O bonds in BO₃ units from meta- and ortho-borate groups [23, 25]. The intensity of this band decreases up to $x = 1$ mol % and after increases and remains the same for $x \geq 5$ mol %.

Chekhovskii [26] assigned the absorption band located at ~ 1340 cm⁻¹ to the B-O asymmetric stretching vibrations in BO₃ and BØ₂O⁻ units. The intensity of this band decreases with the increasing of MnO content up to $x = 1$ mol % and after increases and remains the same for $x \geq 5$ mol %. It can be remarked that the addition of manganese ions in the vitreous matrix determines the decreasing of tricoordinated boron ions up to ~ 1 mol % then their increasing for $x \geq 5$ mol %.

It must be remark that the band corresponding to the FT-IR absorptions of MnO was not evidenced directly for all studied glasses. The manganese addition in the glasses affected relatively little the network structure, as it can be seen from Fig. 1, the intensity of the absorption bands in the manner that depends of these bands. These data evidenced that the formed structure of 2Bi₂O₃·B₂O₃ glass matrix is relatively stable.

Table 1. Assignments of the FT-IR and Raman absorption bands of $x\text{MnO} \cdot (100-x)[2\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ glasses to specific structural groups.

Wavenumber (cm ⁻¹)		FT – IR assignment	Raman assignment
FT - IR	Raman		
	~ 210		Bi-O bonds vibrations in BiO ₃ and distorted BiO ₆ units
	~ 360		Bi-O-Bi stretching vibrations in distorted BiO ₆ octahedral units
~ 480		Stretching vibrations of Bi-O bonds in strongly distorted BiO ₆ units, B-O-B bonds bending vibrations, Specific vibrations of Mn-O bonds	
~540	~ 588	Bi-O bonds stretching vibrations in distorted BiO ₆ units	Stretching vibrations of Bi-O ⁻ in BiO ₆ units, Vibrations of ring type metaborate groups
~720	~ 730	Symmetric stretching vibrations of Bi-O bonds in BiO ₃ units, O ₃ B-O-BO ₃ bending vibrations	Vibrations of chain type metaborate groups
~873		Symmetric stretching vibrations of Bi-O bonds in the BiO ₃ units, Stretching vibrations of B-O bonds in BO ₄ units from diborate groups	
	~ 935		Vibrations of orthoborate groups
~ 1030		Stretching vibrations of B-Ø bonds in BØ ₄ units from tri-, tetra- and penta-borate groups	
~ 1190		Stretching vibrations of B-O bonds in BO ₃ units from meta- and ortho -borate groups	
	~ 1230		Symmetric stretching vibrations of terminal B-O ⁻ bonds in pyroborate groups
~ 1340		Asymmetric stretching vibrations of B-O bonds in BO ₃ and BØ ₂ O ⁻ units	
	~ 1598		B – O ⁻ bonds stretching vibrations involving nonbridging oxygen in various borate groups

Ø - Oxygen atom bridging two boron atoms

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 are placed in BiO₃

pyramids and BiO_6 distorted octahedron, which were detected from its characteristic Bi-O bonds infrared vibrations, also the boron ions are placed in BO_3 (infrared absorption present in the range $1100\text{-}1400\text{cm}^{-1}$) and BO_4 (infrared absorption present in the range $800\text{-}1100\text{cm}^{-1}$) 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 $\sim 480\text{cm}^{-1}$) and BiO_3 (centered at $\sim 720\text{cm}^{-1}$) units and those of B - O bonds vibrations in BO_3 units (present in range $\sim 1190\text{cm}^{-1}$ and $\sim 1340\text{cm}^{-1}$), the BO_4/BO_3 ratio being sub unit.

3.2. Raman data

The Raman spectra of $x\text{MnO}\cdot(100-x)[2\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3]$ glass system, with $0 \leq x \leq 35$ mol % are presented in figure 2 and the assignments of the detected absorption bands are summarized in table 1. In the glass matrix spectrum, the following bands are present: $\sim 210\text{cm}^{-1}$, $\sim 360\text{cm}^{-1}$, $\sim 588\text{cm}^{-1}$, $\sim 730\text{cm}^{-1}$, $\sim 935\text{cm}^{-1}$ and $\sim 1230\text{cm}^{-1}$.

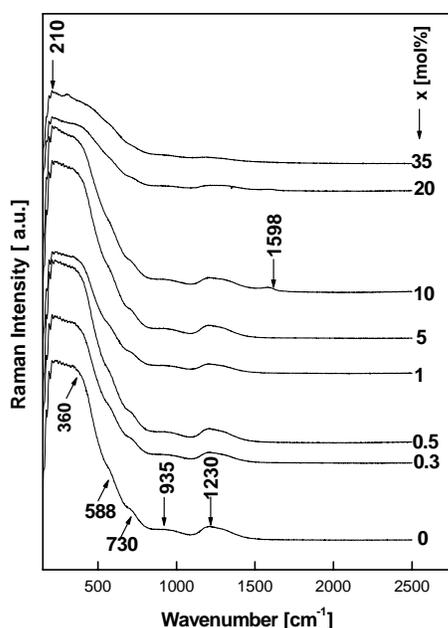


Fig. 2. Raman spectra of $x\text{MnO}\cdot(100-x)[2\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3]$ glasses.

In the spectral range $200\text{-}400\text{cm}^{-1}$ are present the most intense and broad bands which confirm the presence in this glass structure of BiO_3 and BiO_6 units. The first band observed in Raman spectra is centered at $\sim 210\text{cm}^{-1}$ and can be attributed to vibrations of Bi-O bonds in BiO_3 and distorted BiO_6 units [27]. The intensity of this band is approximately the same for all compositional range studied. The band centered at $\sim 360\text{cm}^{-1}$ can be attributed to the Bi-O-Bi stretching vibrations in distorted BiO_6 octahedral units [27]. This band is increasing for samples

up to 10 mol% then for higher concentration decreases gradual with the increasing of the manganese ions content.

The weak shoulder centered at $\sim 588\text{cm}^{-1}$ can be attributed to the stretching vibrations of Bi - O bonds in BiO_6 units [27] and vibrations of ring type metaborate groups [21, 28-30]. The addition of manganese ions in the glass matrix involves a decreasing in the intensity and for samples with $x = 35$ mol% this shoulder disappear.

The weak shoulder centered at $\sim 730\text{cm}^{-1}$ indicates the presence of vibrations of chain type metaborate groups [28-32]. The intensity of this shoulder decreases with the increasing of MnO content.

The presence of vibrations of ortoborate groups are indicated by the band centered at $\sim 935\text{cm}^{-1}$ [28-30]. This band is present in the studied glasses for $x \leq 10$ mol % and has the same intensity.

At $\sim 1230\text{cm}^{-1}$, for samples with $0 \leq x \leq 20$ mol %, the Raman spectra show a band which can be attributed to the symmetric stretching vibrations of terminal B-O bonds in pyroborate groups [31]. The intensity of this band remains the same for $x \leq 10$ mol % and for higher concentrations it decreases. For sample with $x = 10$ mol % appears a new band centered at $\sim 1598\text{cm}^{-1}$, which can be attributed to the B - O stretching vibrations involving nonbridging oxygen (NBO) in various borate groups [17, 32, 33].

In the Raman spectra it can be observed that the addition of MnO oxide produces some changes in the structure of studied glasses. These spectral data evidence that the bismuth ions are incorporate in the glass network as BiO_3 and BiO_6 polyhedra and the boron ions are incorporate in various structural borate groups. The presence of these structural units in the studied glasses depends on the MnO content, but the presence of Mn-O specific vibrations was not directly evidenced. From the shape of Raman spectra results that the studied glasses become more distorted for $x \geq 20$ mol %.

4. Conclusion

Several homogeneous glasses of the $x\text{MnO}\cdot(100-x)[2\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3]$ system were obtained in the range $0 \leq x \leq 50$ 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 manganese ions as modifier of the glass network. The FT - IR studies indicates the presence in structure of the studied glasses of BiO_3 , BiO_6 , BO_3 and BO_4 units, but their proportion depends of the presence of manganese 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 $x \geq 20$ mol%, the structure of the studied glasses become more disordered. The presence of manganese ions in $2\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ glass matrix was not directly evidenced by FT-IR and Raman measurements, only their influence on formation and distribution of different bismuth and boron structural units.

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