

Structural investigation of the $x\text{V}_2\text{O}_5(1-x)[\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3]$ glasses by IR absorption, EPR and NMR

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The aim of structural characterization of the $\text{V}_2\text{O}_5 - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$ glassy system is to clarify the role played by the Bi_2O_3 as an unconventional network former in the structure of the investigated samples. FT-IR absorption spectra present the vibration frequencies characteristic to the both Bi_2O_3 and B_2O_3 , and, also, the influence of vanadium pentaoxide on the main IR absorption bands. The presence of the main structural units $[\text{BiO}_3]$, $[\text{BiO}_6]$, $[\text{BO}_3]$ and $[\text{BO}_4]$ and their dependence on the V_2O_5 content is evidenced. The EPR (Electron Paramagnetic Resonance) spectra contain a single resonance line centered at $g \approx 1.98$ with a partially resolved ^{51}V ($I=7/2$) hyperfine structure for the samples with high V_2O_5 content ($x > 30$ mol %). This fact reveals the existence of the isolated paramagnetic V^{4+} ions, whose resonance line overlaps the broad line characteristic to the associated V^{4+} ions (for $1 \leq x \leq 20$ mol %). ^{11}B MAS-NMR (Magic Angle Spinning Nuclear Magnetic Resonance) spectra performed on the studied glass samples indicate the changes produced by the addition of vanadium pentaoxide on the coordination of boron atoms. The modification of the relative intensity and position of the resonance lines corresponding to the boron atoms suggests the influence of V_2O_5 on the local structure of the studied glasses.

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1. Introduction

Glasses belong to the class of materials characterized by short range order, this fact providing them specific properties. One of the most common approach to study the glass structure is the inclusion of paramagnetic ions (as V_2O_5 , CuO , Fe_2O_3), in the vitreous matrix, the resulting multi-component glasses being analyzed using spectroscopic methods, such as IR absorption, Raman, EPR and NMR. The transitional metal ions are used because they have an incomplete 3d orbital with a broad radial distribution function and they are very sensitive to the surrounding of the cations. Bi_2O_3 is known as an unconventional glass former and is characterized by a high polarizability and density. The addition of Bi_2O_3 to the traditional glass former B_2O_3 improves the chemical durability and thermal stability of the samples [1].

On the last several years the interest of studying the glasses based on Bi_2O_3 as an unconventional network former has been increased, due to their special optical properties. Heavy-metal oxide (HMO) glasses might be arbitrarily defined as those glasses containing over 50 cation percent of bismuth and/or less which participate in the glass structure as network formers. They are characterized by high density, high refractive index, high thermal expansion, and excellent infrared transmission [2]. Since network bond strengths of HMO glasses are relatively weak compared to those of silicate and borate glasses, the glass-forming regions are limited, particularly if none traditional formers are present. The literature

reports several HMO glasses which have been formed by the fast quenching of melts.

In the present work, the vanadium ion V^{4+} present in the vanadyl (VO^{2+}) group is used as a spectroscopic probe for investigation the local structure of $\text{V}_2\text{O}_5 - \text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$ glass system.

2. Experimental

The analytical grade reagents of V_2O_5 , Bi_2O_3 and H_3BO_3 were used as starting materials for preparing the samples. The right amounts of starting oxides that form the vitreous system $x\text{V}_2\text{O}_5 \cdot (100-x)[\text{Bi}_2\text{O}_3\cdot\text{B}_2\text{O}_3]$, with $0 \leq x \leq 50$ mol %, were calculated. Then, the appropriate quantities of oxides were ground in a mortar and the resulting homogeneous mixture was melted at 1250°C for 6 minutes in an electrical furnace. The molten liquid was poured onto a cooper plate and pressed with another one very quickly.

The FT-IR spectra were recorded at room temperature, using a Equinox 55 Bruker spectrometer. The followed procedure begins with the preparation of KBr pellets in which a 2 mg amount of glass sample was added. All the IR absorption spectra were recorded at the same experimental conditions.

The EPR spectra were recorded at room temperature in the X-band ($\nu \approx 9.4$ GHz) using a Portable Adani PS 8400 spectrometer.

The NMR spectra of the samples with $x = 0, 1, 30$ and 50 mol % V_2O_5 were recorded using an Avance 400 MHz UltraShield™ Bruker spectrometer.

3. Results and discussion

3.1. IR absorption spectroscopy

As a starting point in order to assign the absorption band in the spectra of the studied glass system, we used the IR absorption spectra of vitreous Bi_2O_3 , B_2O_3 and V_2O_5 [3].

The vitreous B_2O_3 spectrum shows a strong absorption band at 1265 cm^{-1} , a weak one at 720 cm^{-1} and also a shoulder at 1400 cm^{-1} [4]. V_2O_5 spectrum exhibits a sharp and very intense band at 1018 cm^{-1} , a more broad one, but also intense at 828 cm^{-1} and an absorption domain with two maxima at 630 and 428 cm^{-1} [5]. Bi_2O_3 spectrum consists in several bands situated at 460 , 830 and 860 cm^{-1} [6].

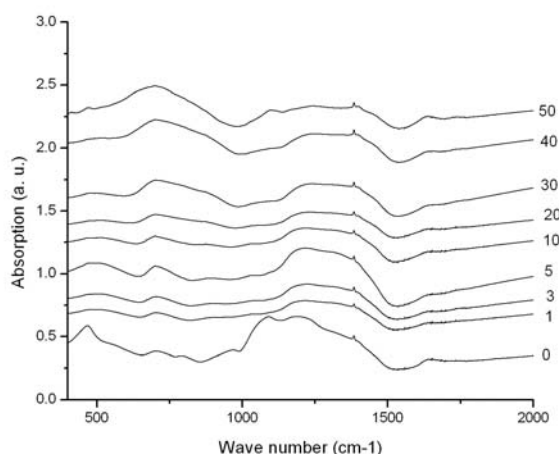


Fig. 1. The IR absorption spectra of the $x\text{V}_2\text{O}_5(100-x)[\text{Bi}_2\text{O}_3/\text{B}_2\text{O}_3]$ glasses.

The IR absorption spectra of the $x\text{V}_2\text{O}_5(100-x)[\text{Bi}_2\text{O}_3/\text{B}_2\text{O}_3]$ system are presented in Fig. 1. These spectra contain absorption bands characteristic to the oxides that form the vitreous matrix, Bi_2O_3 and B_2O_3 . The evolution of the spectra with increasing the content of V_2O_5 shows how this oxide takes place at the structure of the samples [7].

First absorption band situated at 460 cm^{-1} is assigned to the Bi – O vibration mode in the $[\text{BiO}_6]$ configuration. Because this band appears only for the samples with $x=0$ and $5\text{ mol } \%$, we assume that only in these two cases the $[\text{BiO}_6]$ structural units participate at the vitreous structure.

The following IR absorption band located at 700 cm^{-1} is changing its position to lower wave numbers, $\sim 695\text{ cm}^{-1}$ while increasing the content of V_2O_5 and is characteristic to the vibrations of distortion of B-O-B chains.

In this spectral region another absorption band also appears and is assigned to the vibrations of $\text{O}_2\text{B-O-BO}_2$ chain. We observe that for $x \geq 30\text{ mol } \%$ V_2O_5 the IR absorption band from 695 cm^{-1} overlaps next band at

820 cm^{-1} , which indicates the presence of pyramidal units $[\text{BiO}_3]$. Because this absorption band is present in all the recorded spectra of the studied samples and over more, its intensity increases, we can assume that the principal structural units that participate at the formation of vitreous network are $[\text{BiO}_3]$ units.

The presence of the boroxol rings is attested by the IR absorption band from 970 cm^{-1} . The intensity of this band is almost constant for the entire concentration domain, with a single exception, the sample with $x=0\text{ mol } \%$ V_2O_5 . When the content of vanadium oxide increases, this absorption band appears at higher wave numbers and overlaps the next one, at 1095 cm^{-1} , assigned to the $[\text{BO}_4]$ structural units. The three coordinated boron exhibits an IR absorption band situated at 1230 cm^{-1} . Making a comparison between the intensities of the bands characteristic to the three or four coordinated boron atoms, we can affirm that the $[\text{BO}_3]$ structural units are predominant and participate directly at the structure of the investigated glass samples.

The absorption band situated at 1380 cm^{-1} is assigned to the stretching vibrations of the B-O bond and also, to the stretching vibrations of the boroxol rings.

The presence of water in the samples is shown by the next absorption band situated at 1635 cm^{-1} , which is a very large band and describes the bending vibrations of H-O-H bond. Because the intensity of this absorption band is very weak made us conclude that the investigated glass samples have a low hygroscopic character.

3.2. Electron Paramagnetic Resonance (EPR)

The EPR spectra are characteristic to those of oxide glass systems which includes vanadium ions, presented as vanadyl ions (VO^{2+}), in a ligand field of C_{4v} symmetry [8].

The spectra presented in Fig. 2 are analyzed using an axial spin Hamiltonian:

$$H = \beta_0 [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y).$$

Analyzing the EPR spectra, a single line centered at $g \approx 1.98$ for the entire range of V_2O_5 content is present. For $1 \leq x \leq 10\text{ mol } \%$ the spectra did not show hyperfine structure and this fact leads to the conclusion that in the studied compositional range more V^{4+} ions are formed, which can be associated, being favoured by the structure of the vitreous matrix,.

For $x \geq 30\text{ mol } \%$ the structure of the matrix allows the formation of associated V^{4+} ions, and isolated V^{4+} ions which in the EPR spectra manifest through a overlap of a signal with a partial resolved hyperfine structure with a broad line characteristic to the associated V^{4+} ions. We considered that this behavior of the V^{4+} ions is determined by the presence of the Bi_2O_3 in the vitreous matrix, because in the borate glasses which contain vanadium [9] the association of these ions is realized at the same time with the increase of the V_2O_5 content.

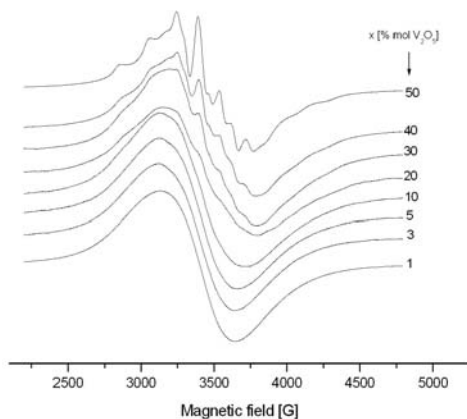


Fig. 2. The EPR spectra of the $x\text{V}_2\text{O}_5(100-x)[\text{Bi}_2\text{O}_3\text{B}_2\text{O}_3]$ glasses.

3.3. Nuclear Magnetic Resonance (NMR)

Solid-state ^{11}B NMR spectroscopy is a very useful technique in the structural characterization of boron-containing glasses, because early work has shown that trigonal $[\text{BO}_3]$ and tetrahedrally coordinated $[\text{BO}_4]$ boron can be distinguished by their ^{11}B quadrupole coupling parameters [10], thereby allowing a determination of the relative fraction of these two boron sites for different materials. For boron containing glasses the $[\text{BO}_3]$ units exhibit isotropic chemical shifts in the range $12 \leq \delta_{\text{iso}} \leq 25$ ppm, and $[\text{BO}_4]$ tetrahedra resonate at lower frequencies in the range $-4 \leq \delta_{\text{iso}} \leq 6$ ppm [11]. Thus, separate resonances for these two boron structural units can be separated using very high magnetic fields ($B \geq 9.4$ T) [12].

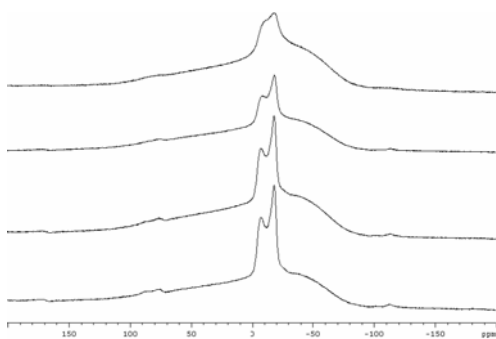


Fig. 3. The ^{11}B MAS-NMR spectra of the $x\text{V}_2\text{O}_5(100-x)[\text{Bi}_2\text{O}_3\text{B}_2\text{O}_3]$ glasses ($x = 0$ – bottom line, $x = 1, 30, 50$ mol% V_2O_5 , the upper lines).

In the MAS-NMR spectra of the studied glassy samples with $x = 0, 1, 30, 50$ mol % V_2O_5 , we can observe that two different resonance lines appear, one at ~ -8 ppm, and the other one at ~ -18 ppm. The former line is characteristic to the $[\text{BO}_4]$ tetrahedra, and the latter one is attributed to the $[\text{BO}_3]$ structural units. The NMR spectra show that the $[\text{BO}_3]$ pyramids are the main structural units which participate in the structure of the investigated samples, the number of the $[\text{BO}_4]$ units decreasing with the increase of V_2O_5 content. The line broadening of the resonance signals is increasing with

increasing the vanadium pentoxide concentration, a fact that made us conclude that the disorder accentuates due to the simultaneous presence of the $[\text{BO}_3]$, $[\text{BO}_4]$, boroxol rings and vanadium ions which break the B – O bonds in the glass network. The ^{11}B MAS NMR data are in very good agreement with IR data, the last one proving the formation of the boroxol rings at high content of V_2O_5 , and also the increasing of disorder in the studied samples, evidenced by the broadening of the spectra characteristic to the high values of V_2O_5 concentration.

4. Conclusions

Investigating the structure of the vitreous system $x\text{V}_2\text{O}_5(100-x)[\text{Bi}_2\text{O}_3\text{B}_2\text{O}_3]$ by FT-IR absorption spectroscopy we can conclude that the main units involved in the formation of glass structure are the pyramids $[\text{BO}_3]$ and $[\text{BiO}_3]$ and the boroxol rings. Increasing the content of V_2O_5 the principal network former is proven to be B_2O_3 .

For $x \leq 30$ mol %, the EPR spectra show a single resonance line centered at $g \sim 1.98$ characteristic to associated V^{4+} ions. For $x \geq 30$ mol% the EPR spectra develop a partially resolved hyperfine structure, a fact that made us conclude that the increase of paramagnetic oxide leads to the formation of isolated V^{4+} ions, decreasing the number of associated V^{4+} ions, which appear at the low concentrations of V_2O_5 . We suppose that this fact is favored by the presence of Bi_2O_3 in the matrix of the studied system.

The ^{11}B MAS-NMR spectra indicate, in agreement with IR absorption spectra, the simultaneous presence of $[\text{BO}_3]$, $[\text{BO}_4]$ structural units, and also, of the boroxol rings. The main contribution to the structure of the investigated samples belongs to the $[\text{BO}_3]$ structural units.

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