

FTIR structural investigation of $3\text{B}_2\text{O}_3\cdot\text{BaO}$ glass matrix containing manganese ions

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The glasses of the system $x\text{MnO}\cdot(100-x)[3\text{B}_2\text{O}_3\cdot\text{BaO}]$ system with $0 \leq x \leq 50$ mol% were prepared and characterized by IR spectroscopy. The influenced of gradual increase in MnO content on the glass structure were revealed. It was estimated the presence and the dependence of the borate structural units by the MnO content. For our system both BO_3 and BO_4 units was detected, the first being dominant in all concentration range.

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1. Introduction

Structural properties of the vitous systems were frequently studied by means of the FT – IR spectroscopy [1].

Glasses are studied nowadays mainly because of the large applications that they span. B_2O_3 is one of the most common glass former and is present in almost all commercially important glasses. It is often used as a dielectric and insulating materials and because of the occurrence of boron anomaly [2]. Barium borate glasses are important because of their use as a non-volatile flux in the crystal growth of garnets and ferrites [3]. The addition of iron oxide to borate glasses makes them electrically semiconducting and superparamagnetic [4].

The borate glasses are very often investigated by a lot of methods because they are relatively easy to obtain and moreover because in their structure appears a large variety of structural units over a wide range of modifier concentration [5, 6].

The structure of borate glasses was studied by X-ray [7,8] and neutron [9,10] diffraction, IR [11], Raman [11-14] and NMR [15-16] spectroscopies. All investigations report that B_2O_3 is composed essentially of BO_3 units forming three-membered (boroxol) rings. The addition of oxides such as BaO results in the change of some BO_3 units in BO_4 units. The introduction of the metal ions such as MnO in glasses produces other changes in glass structure.

In this paper we proposed to study by means of FTIR spectroscopy the structural modification in the $3\text{B}_2\text{O}_3\cdot\text{BaO}$ glass matrix by gradual increasing of MnO content.

2. Experimental

Glasses from the $x\text{MnO}\cdot(100-x)[3\text{B}_2\text{O}_3\cdot\text{BaO}]$ system were prepared using reagent grade purity MnCO_3 , H_3BO_3 , and BaCO_3 in suitable proportions. The mechanically homogenized mixtures were directly introduced and

melted in sintered corundum crucibles at 1250°C for 30 minutes, in an electrical furnace. The melts were poured onto stainless steel plates.

The X-ray patterns of the investigated samples are characteristic for the vitreous systems. No crystalline phases were observed up to 50 mol% MnO.

The FT-IR absorption spectra of the glasses in the $400 - 2000\text{ cm}^{-1}$ spectral range were obtained with an Equinox 55 Bruker spectrometer. The measurements were done using the KBr pellet technique. The samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture.

3. Results and discussion

The experimental IR spectra of the $x\text{MnO}\cdot(100-x)[3\text{B}_2\text{O}_3\cdot\text{BaO}]$ glass system, with $0 \leq x \leq 50$ mol% , are presented in Fig. 1. The obtained absorption bands and their assignments are summarized in Table 1.

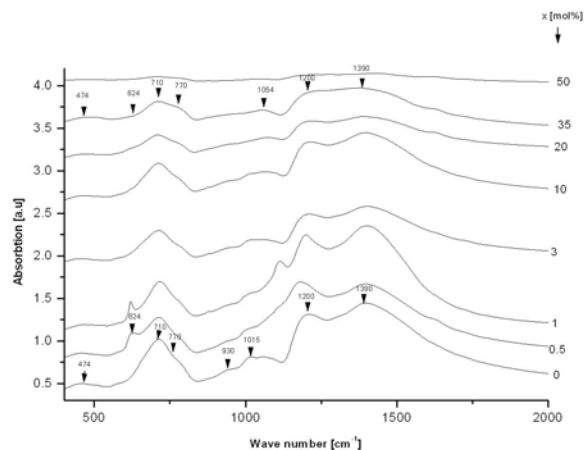


Fig. 1. Infrared absorption spectra of $x\text{MnO}\cdot(100-x)[3\text{B}_2\text{O}_3\cdot\text{BaO}]$ glasses.

Table 1. Frequencies and their assignments for IR spectra of $x\text{MnO} \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot \text{BaO}]$ glasses.

Wavenumber (cm ⁻¹)	Assignment
~ 474	Specific vibrations of Ba-O bonds
~624	Specific vibrations of Mn-O bonds
~ 709	B-O-B bending vibrations
~ 770	O ₃ B-O-BO ₄ bending vibrations
~ 930 ~ 1015 ~ 1054	B-O stretching vibration of BO ₄ units in tri-, tetra- and penta- borate groups
~ 1200	B-O stretching vibration of trigonal BO ₃ units in boroxol rings
~ 1390	B-O stretching vibrations of BO ₃ units in meta-, pyro- and ortho-borate groups.

For the interpretation of the results we used the Tarte [17, 18] and Condrate [19, 20] methods. The experimental data are compared with those obtained for crystalline samples. In our studied we used the absorption bands of the crystalline manganese oxides MnO_2 and Mn_3O_4 and BaO [21], and of the vitreous B_2O_3 [22-28].

In the matrix spectrum, the following bands are evidenced: ~ 474 cm⁻¹, ~ 710 cm⁻¹, ~ 770 cm⁻¹, ~ 930 cm⁻¹, ~ 1015 cm⁻¹, ~ 1200 cm⁻¹ and ~ 1390 cm⁻¹.

The band at ~ 1390 cm⁻¹ was assigned to B-O stretching vibrations of trigonal (BO₃) units in metaborate, pyroborate and ortoborate groups [23]. The intensity of this band is decreasing with the increasing of MnO content. The absorption band at ~ 1200 cm⁻¹ was assigned to B-O stretching vibrations of trigonal (BO₃) units in boroxol rings [24]. The intensity of this band increases with the increase of MnO content up to 1 mol%; for higher concentrations, the amplitude of this band decreases and .

The weak bands evidenced at ~ 1054 cm⁻¹, at ~ 1015 cm⁻¹ and at ~ 930 cm⁻¹ was assigned to stretching vibrations of B-O bonds of BO₄ units from tri-, tetra- and penta- borate groups [24-25]. The band at ~ 1015 cm⁻¹ gradually disappears with the increase of MnO content by mearing into band centred at ~ 1054 cm⁻¹. These bands are enough to weak comparatively with those evidenced at ~ 1390 cm⁻¹ and at ~ 1200 cm⁻¹. Therefore, threefold boron atoms are favored in studied glasses compared with fourfold ones.

The band at ~ 770 cm⁻¹ is assigned to the B-O-B bending vibration of bridges containing one trigonal and one tetrahedral boron [24] and has approximately the same intensity for all the compositional range.

In all the IR spectra appears a band at ~ 710 cm⁻¹ relative to the band at ~ 720 cm⁻¹ from the spectrum of vitreous B_2O_3 , which is due to the bending vibration of B-O-B linkage in borate network [22, 26-28]. The intensity of this band increases with the increase of MnO content up to 10 mol%; for higher concentrations, the amplitude of this band decreases.

The band at ~ 624 cm⁻¹ is due to specific vibrations of Mn-O bonds and the band at ~ 474 cm⁻¹ to specific

vibration of Ba-O bonds. It can be noticed that the intensity of the band at ~ 624 cm⁻¹ increases with the increase of MnO content up to 5 mol% and for higher concentrations of MnO almost disappears, while the intensity of the band at ~ 474 cm⁻¹ is approximately the same for all compositional range.

It is remarkable that the presence of high content of $3\text{B}_2\text{O}_3 \cdot \text{BaO}$ glass matrix determine strong structural modification of glass network, behaviour which is specific only for manganese ions.

In case of studied glasses the intensity of absorption bands became large and the bands broaden with the increase of the MnO content. It means that the structure of the studied glasses became disordered. Probably, due to this fact for these concentrations it was not evidenced clearly the absorption in IR of MnO and BaO specific vibrations.

4. Conclusions

Homogeneous glasses of the $x\text{MnO} \cdot (100-x)[3\text{B}_2\text{O}_3 \cdot \text{BaO}]$ system were obtained within $0 \leq x \leq 50$ mol%. IR spectra of these glasses have been analyzed in order to identify the spectral contribution of each component on the structure and to point out the role of the manganese ions as a modifier of the glass network. The shape of the spectrum revealed a significant disorder in our glasses for higher content of MnO.

In the investigated glass system the three-fold boron atoms are dominated compared with the fourfold ones.

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