Preparation and structural characterization of some Fe$_2$O$_3$-B$_2$O$_3$-ZnO glasses and glass ceramics

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Abstract. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy have been employed to investigate the (Fe$_2$O$_3$)$_x$(B$_2$O$_3$)$_{60-x}$(ZnO)$_{40}$ samples, with 0 ≤ x ≤ 20 mol%. The samples have been prepared by melting at 1100 °C for 10 minutes followed by rapid cooling at room temperature. The structure of samples was analyzed by means of XRD. XRD pattern show that the sample without iron ions and the samples contained 3 and 5 mol% were glasses. For samples contain 10, 15 and 20 mol% Fe$_2$O$_3$ it obtains glass ceramics. These glass ceramics contains a unique crystalline phase, zinc ferrite (ZnFe$_2$O$_4$), embedded in an amorphous matrix. FTIR spectroscopy data suggest that for the glass samples the iron ions play the network modifier role. These data show that the glass network consists of BO$_3$ and BO$_4$ structural units. For glass ceramics samples FTIR spectra show characteristic bands of ZnFe$_2$O$_4$.

1. Introduction
Zinc borate glasses exhibit low melting temperatures, so they are of technological interest owing to their applications in different fields of electronic products [1-4]. This is due to the fact that the higher the polarizability of an ion, the lower the melting temperature of the substance. Low melting glasses have been widely used for lowering the sintering temperature and optimizing coefficient thermal expansion in the field of electronic devices such as multi layer ceramic capacitor, low temperature co-fired ceramics, plasma display panels, cathode ray tube, electric modules, etc. [1-4]. On the other hand iron ions have strong bearing on electrical, optical and magnetic properties of glasses. In general the present of iron ions in glasses are considered to assemble together and form clusters which exhibit super paramagnetic behaviour and below the freezing temperature, individual spins are frozen in random directions because of antiferomagnetic interaction between nearby ions [5-8]. A general condition for semiconducting behaviour of borate glasses containing iron ions is the coexistence of iron ions in more than one valence state, Fe$^{2+}$ and Fe$^{3+}$ [6]. Having in view that the addition of iron ions in glasses usually induces significant changes in their magnetic, electric and optical behaviour, opening thus opportunities in the finding of new applications, the careful structural investigations of glasses containing Fe$_2$O$_3$ becomes necessary. The purpose of the present work was to investigate by
XRD and FTIR spectroscopy measurements the zinc borate glasses and glass ceramics containing Fe₂O₃ in order to establish the crystallization behaviour and the structural changes induced by iron oxide addition in these samples.

2. Experimental

Samples of the (Fe₂O₃)ₓ(B₂O₃)₆₀₋ₓ(ZnO)₄₀ system were prepared using Fe₂O₃, H₃BO₃ and ZnO of high purity (99.9%) in suitable proportion. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 1100 °C, in an electric furnace. The samples were put into the electric furnace at the mentioned temperature. After 10 minutes, the molten material was quenched at room temperature by pouring onto a stainless-steel plate.

The X-Ray diffraction measurements of the samples were made with a XRD – 6000 Shimadzu diffractometer, with a monochromator of graphite for Cu Kα radiation (λ = 1.54 Å) at room temperature.

The FTIR absorption spectra of the samples in the 360-1600 cm⁻¹ spectral range were obtained with a JASCO FTIR 6200 spectrometer. The IR absorption measurements were done using the KBr pellet technique. In order to obtain good quality spectra 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. Result and discussion

3.1. XRD data

The XRD patterns of (Fe₂O₃)ₓ(B₂O₃)₆₀₋ₓ(ZnO)₄₀ samples with various content of iron oxide (0 ≤ x ≤ 20 mol%) are presented in figure 1.

![Figure 1. The XRD patterns of the (Fe₂O₃)ₓ(B₂O₃)₆₀₋ₓ(ZnO)₄₀ samples.](image)

These patterns show that for the samples containing 0, 3 and 5 mol% Fe₂O₃ amorphous phase is present. Crystalline phase is not detected but is possible to be in small quantity. For sample containing 10 mol% Fe₂O₃ a small amount of crystalline phase appears which grow up as the content of iron ions increases. For sample containing 20 mol% Fe₂O₃ the crystalline phase becomes a majority one. The crystalline phase was identified as being ZnFe₂O₄ which crystallizes in a cubic system. Lattice
parameter increases with increasing of iron ions content from a = 8.293 Å for sample with 10 mol% Fe$_2$O$_3$ at a = 8.319 Å for sample containing 15 mol% Fe$_2$O$_3$ and respectively at a = 8.381 Å for sample containing 20 mol% Fe$_2$O$_3$.

3.2. FTIR data
The experimental FTIR spectra of (Fe$_2$O$_3$)$_x$·(B$_2$O$_3$)$_{(60-x)}$·(ZnO)$_{40}$ samples with various content of iron oxide (0 ≤ x ≤ 20 mol%) were presented in figure 2. Obtained bands and their assignments are summarized in table 1.

![Figure 2. The FTIR spectra of the (Fe$_2$O$_3$)$_x$·(B$_2$O$_3$)$_{(60-x)}$·(ZnO)$_{40}$ samples.](image)

FTIR spectrum of studied samples contains all the important bands of vitreous B$_2$O$_3$, but shifted from their original position. So, in all FTIR spectrum there is an intense band at 680-685 cm$^{-1}$ from vitreous IR spectrum of B$_2$O$_3$ and is attributed to B–O–B bending vibrations [9-12]. The intensity of this band decreases with the increasing of Fe$_2$O$_3$ concentration. The absorptions from around 875 cm$^{-1}$ can be attributed to the stretching vibrations of B–O bonds in BO$_4$ units from diborate groups [9-12] and the band from around 1050 cm$^{-1}$ is attributed to the stretching vibrations of B–O bonds in BO$_4$ units from tri-, tetra- and penta-borate groups [9-12].

Table 1. Wavenumbers and their assignments for FTIR spectra of (Fe$_2$O$_3$)$_x$·(B$_2$O$_3$)$_{(60-x)}$·(ZnO)$_{40}$ samples.

| Wavenumber (cm$^{-1}$) | Assignment |
|------------------------|------------|
| 430-455                | The vibration of the chemical bond (Fe$^{3+}$–O$^2-$) in B location of the octahedron |
| 560-585                | The vibration of the chemical bond (Zn$^{2+}$–O$^{2-}$) in A location of the tetrahedron |
| 680-685                | B-O-B bending vibrations |
| 875                    | B-O stretching vibrations of tetragonal (BO$_4$) units in di-borate groups |
| 1050                   | B-O stretching vibrations of tetragonal (BO$_4$) units in tri-, tetra- and penta-borate groups |
| 1250                   | B-O stretching vibrations of trigonal (BO$_3$) units in boroxol rings |
| 1390-1400              | B-O’ stretching vibrations of trigonal (BO$_3$) units in different borate groups |
The intensity of these bands is increasing with the increasing of iron ions content. The absorption band from around 1250 cm\(^{-1}\) is attributed to the asymmetric stretching vibrations of B–O bonds in BO\(_3\) units from in boroxol rings [9-12] and the band from 1390-1400 cm\(^{-1}\) was attributed to the stretching vibrations of B–O in BO\(_3\) units from different borate groups [9-12]. The intensity of this band increases with the increasing of Fe\(_2\)O\(_3\) concentration till 15 mol\%, and for higher concentrations the intensity of this band decreases. The presence of ZnFe\(_2\)O\(_4\) in studied samples for x > 10 mol% is confirmed by the appearances of two absorption peaks. That of sample containing 15 mol\% Fe\(_2\)O\(_3\) appears at around 585, 445 cm\(^{-1}\), and that of sample containing 20 mol\% Fe\(_2\)O\(_3\) at around 560, 430 cm\(^{-1}\), which are basically consistent with the literature [12]. The two strong absorption peaks are attributed to the vibration of the chemical bond (Zn\(^{2+}\)–O\(^{2-}\)) in A location of the tetrahedron and the vibration of the chemical bond (Fe\(^{3+}\)–O\(^{2-}\)) in B location of the octahedron respectively [12]. The intensity of these bands increases with the increasing of iron ions content.

4. Summary
Homogeneous glasses of the (Fe\(_2\)O\(_3\))\(_x\)·(B\(_2\)O\(_3\))(60-x)·(ZnO)\(_{40}\) system were obtained within 0 ≤ x ≤ 5 mol\%. For x = 10, 15 and 20 mol\% the XRD patterns shows that were obtained glass ceramics with contain a unique crystalline phase, identified as been ZnFe\(_2\)O\(_4\), which crystallizes in a cubic system. Lattice parameter increases with increasing of iron ions content from a = 8.293 Å for x = 10 mol\% at a = 8.381 Å for x = 20 mol\%.

The FTIR study shows that B\(_2\)O\(_3\) play the network former role and the iron ions play a network modifier role in the studied samples. The glasses network consists of BO\(_3\) and BO\(_4\) structural units. From FTIR spectra, the bands from 430-455 cm\(^{-1}\) and from 560-585 cm\(^{-1}\) confirm the presence of ZnFe\(_2\)O\(_4\).

Acknowledgements
This work was supported by a Grant of Romanian Ministry of Research and Education, CNCSIS PNII-IDEI 226/ 2008 grant.

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