Structural study of the Fe_2O_3-B_2O_3-BaO glass system by FTIR spectroscopy

M. TODERAŞ[a,b*], S. FILIP[a], I. ARDELEAN[b]

[a]Department of Physics, University of Oradea, Oradea, Romania
[b]Faculty of Physics, Babeş-Bolyai University, Cluj-Napoca, Romania

Glasses belonging to the $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot BaO]$ system, with $0 \leq x \leq 50$ mol% were prepared and characterized by IR spectroscopy. It was establised the mode in wich Fe_2O_3 influence the local structure of the $3B_2O_3 \cdot BaO$ glass matrix. The IR absorption data indicate that the BO_4 / BO_3 ratio in the studied glasses is dependent on the iron ions content.

1. Introduction

IR spectroscopy is a very sensitive and one of the most used spectroscopy metods applied in the investigation of the local structure characterizing vitreous materials like oxide glasses [1].

The borate glasses are very often investigated because they are relatively easy to obtain and, moreover, in their structure appears a large variety of structural units over a wide range of modifier concentration [1,2]. Borate glasses are scientifically interesting because of the occurrence of the boron anomaly [3] and for their application as a dielectric material. The presence of some transitional metal ions in the glass structure makes the glass electrically semiconducting and superparamagnetic [4].

The structure of B_2O_3 glass has been studied by a lot of structural methods [5 – 14]. All studies suggest that in the pure B_2O_3 glass the boron atoms are three fold coordinated, the basic structural unit consisting in a boroxol ring B_2O_6. The addition of glass modifier oxide changes the coordination of boron from 3 to 4 as a result of BO_4 units formation [15 – 17].

The aim of this paper is to present the structural information obtained on the $3B_2O_3 \cdot BaO$ glass matrix containing Fe_2O_3 by means of FTIR spectroscopy measurements.

2. Experimental

Samples of $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot BaO]$ glass system were prepared. For the preparation chemical pure raw materials were used: Fe_2O_3, H_3BO_3, and $BaCO_3$ in suitable proportions. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 1250 °C, in an electrical furnace. The samples were put into the electric furnace direct at this temperature. After 30 minutes, the molten material was quenched at room temperature by pouring onto a stainless–steel plate. The samples were analyzed by means of X-ray diffraction and did not show any crystalline phase up to 50 mol% Fe_2O_3.

The FT-IR absorption spectra of the glasses in the $400 – 2000$ cm^{-1} spectral range were obtained with an Equinox 55 Bruker 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. Results and discussion

The experimental IR spectra of the $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot BaO]$ glass system (Fig. 1) were compared with those coresponding to vitreous B_2O_3 [18 - 24] and crystalline BaO, Fe_2O_3 [25] oxides. Obtained absorbtion bands and their assignments are summarized in Table 1.

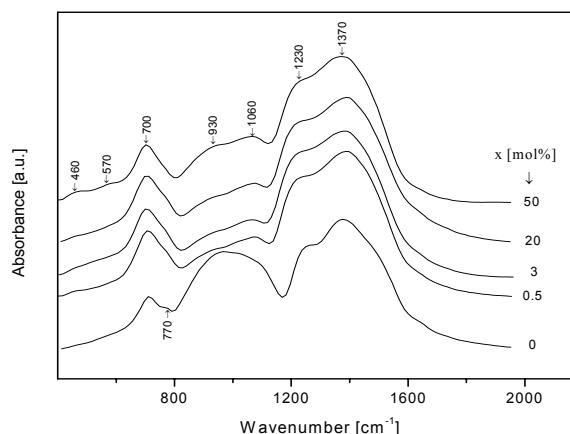*Fig. 1. Infrared absorption spectra of*
$xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot BaO]$ glasses.

Table 1. Frequencies and their assignments for IR spectra of $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot BaO]$ glasses.

Wavenumber (cm^{-1})	Assignment
~ 460	Specific vibrations of Fe-O and Ba-O bonds
~ 570	Specific vibrations of Fe-O and Ba-O bonds
~ 700	B-O-B bending vibrations
~ 770	O_3B-O-BO_4 bending vibrations
~ 930 ~ 1060	B–O stretching vibration of BO_4 units in tri-, tetra- and pentaborate groups
~ 1230	B–O stretching vibration of B-O bond of BO_4 units from boroxol rings
~ 1370	B-O stretching vibrations of BO_3 units in metaborate, pyroborate and ortoborate groups.

The IR spectrum of the vitreous B_2O_3 [18-19] contains a intense absorption bands at ~ 1400 cm^{-1} and at ~ 1265 cm^{-1}, a lowest absorption band at ~ 720 cm^{-1}. Barium crystalline oxide BaO presents an intense band at ~ 483 cm^{-1} and a low one at ~ 503 cm^{-1} [19 - 25]. Iron crystalline oxide αFe_2O_3 presents an intense band at ~ 468 cm^{-1} and a large intense band at ~ 560 cm^{-1} [19 - 25]. For γFe_2O_3 were identified two lowest absorption bands at ~ 468 cm^{-1} and ~ 555 cm^{-1} [19 -25].

The bands at ~ 460 cm^{-1} and ~ 570 cm^{-1} are assigned to specific vibrations of Fe-O bonds [19 -25], over wich can be superposed the contribution of the Ba-O bonds [25]. The intensity of these bands are very weak in all concentration range studied.

In all the IR spectra a strong band appears at ~ 700 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 linkages in borate network [20]. The intensity of this band increases with the increase of Fe_2O_3 content up to 3 mol%. For higher concentrations, the amplitude of this band decreases very small. The band at ~ 770 cm^{-1} is assigned to the B-O-B bending vibration of bridges containing one trigonal and one tetrahedral boron [21]. This band are evidenced only in the glass matrix $3B_2O_3\cdot BaO$ (x=0). The bands at ~ 930 cm^{-1} and at ~ 1060 cm^{-1} was assigned to B-O stretching vibration BO_4 units in tri-, tetra- and penta- borate groups [21-24]. The intensity of these bands is very large in the glass matrix (x=0). For x=0.5 mol% the amplitude of these band decreases and for higher concentrations of Fe_2O_3 they increase. The absorption band at ~ 1230 cm^{-1} was assigned to B–O stretching vibration of trigonal BO_3 units in boroxol rings [20]. The intensity of this band increases with the increase of Fe_2O_3 content up to 3 mol% and after very small. The band at ~ 1370 cm^{-1} was assigned to B-O stretching vibrations of BO_3 units in meta-, pyro- and orto- borate groups [21-24]. The intensity of this band increases up to x=0.5 mol% and thereafter, remains almost the same in all the compositional range. For all compositional range the bands at ~1230 cm^{-1} and ~1370 cm^{-1} are more intense than the bands at ~ 930 cm^{-1} and ~1060 cm^{-1}. This result suggests that in the studied glasses the threefold boron atoms are dominant if compared with the fourfold ones.

From this study it was concluded that the presence of the iron ions in the glass matrix determines the modification of the BO_4 / BO_3 ratio, but has not large influence on structural disorder of glass matrix.

4. Conclusions

Homogeneous glasses of the $xFe_2O_3\cdot(100\text{-}x)[3B_2O_3\cdot BaO]$ system were obtained within $0 \leq x \leq 50$ mol% composition range.

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 iron ions as a modifier of the glass network.

The bands at ~ 460 cm^{-1} and at ~ 570 cm^{-1} confirm the presence of the iron and barium ions in our glasses. The threefold boron atoms are favored in the investigated glass system compared to the fourfold ones.

References

[1] J. Wong, C. A. Angell, Glass Structure by Spectroscopy, M. Dekker Inc., New York, 1976.

[2] E. I. Kamitos, J. A. Kapoutsis, H. Jain, C. H. Hsieh, J. Non-Cryst. Solids **171**, 31 (1994).

[3] D. L. Griscon, Material Science Research, Borate Glasses 12 (Plenum, New York, 1978).

[4] D. W. Moon, A. J. M. Aitken, R. K. MacCrone, C. S. Cieloszyk, Phys. Chem. Glasses **16**, 91 (1975).

[5] R. L. Mozzi, B. E. Warren, J. Appl. Crystallogr. **3**, 251 (1970).

[6] E. Chason, F. Spaepen, J. Appl. Phys. **64**, 4435 (1988).

[7] A. C. Hannon, R. N. Sinclair, J. A.Blackman, A. C. Wright, F. L. Galeener, J. Non-Cryst. Solids, **106**, 116 (1988).

[8] A. C. Wright, R. N. Sinclair, D. I. Crimley, R. A. Hilme, N. M. Vedishcheva, B. A. Shakhmathin, A. C. Hannon, S. A. Feller, B. M. Meyer, M. L. Royle, D. L. Wilkerson, Glass Phys. Chem. **22**, 268 (1996).

[9] F. L. Galeener, J. Non-Cryst. Solids **40**, 527 (1980).

[10] G. E. Walrafen, S. R. Samanta, P. N. Krishnan, J. Phys. Chem. **72**, 113 (1980).

[11] T. Furukawa, W. B. White, Phys. Chem. Glasses **21**, 85 (1980).

[12] C. F. Windisch Jr., W. M. Risen Jr., J. Non-Cryst. Solids **48**, 307 (1982).

[13] G. E. Jellison Jr., L. W. Panek, P. J. Bray, G. B. Rouse Jr., J. Chem. Phys. **66**, 802 (1977).

[14] P. J. Bray, S. A. Feller, G. E. Jellison Jr., Y. H. Yun, J. Non-Cryst. Solids **38&39**, 93 (1991).

[15] D. R. Uhlmann, R. R. Shaw, J. Non-Cryst. Solids **1**, 347 (1969).

[16] W. L. Konijnendijk, J. M. Stevels, J. Non-Cryst. Solids **18**, 307 (1975).

[17] B. N. Meera, J. Ramakrishna, J. Non-Cryst. Solids **159**, 1 (1993).

[18] G. Fuxi, Optical and Spectroscopic Properties of Glass, Springer-Verlag, Shanghai Scientific Technical Pub., Shanghai, 1991.
[19] A. S. Tenny, J. Wong, J. Non-Cryst. Solids **56**, 5516 (1972).
[20] I. Ardelean, F. Ciorcas, M. Peteanu, I. Bratu, V. Ioncu, Mod. Phys. Lett. B **14**, 653 (2000).
[21] E. I. Kamitsos, M. A. Karakassides, G. D. Cryssikos, J. Phys. Chem. **91**, 1073 (1987).
[22] S. G. Motke, S. P. Yawale, S. S. Yawale, Bull. Mater. Sci. **25**, 75 (2002).

[23] I. Ardelean, Monica Toderas, P. Pascuta, Mod. Phys. Lett. B **17**, 1175 (2003).
[24] I. Ardelean, P. Pascuta, Mod. Phys. Lett. B **16**, 539 (2002).
[25] F. F. Bentley, L. D. Smithson, A. L. Rozek, Infrared Spectra and Characteristic Frequencies 700-300 cm^{-1}, Interscience, New York, 1968.

_____

[*]Corresponding author: atoderas@uoradea.ro