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FTIR spectra of glasses from BaO-B_2O_3-TiO_2 system

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Glasses in the BaO-B_2O_3-TiO_2 system were obtained by melting and ultra fast quenching to avoid crystallization. Melting temperatures were in the range 1100-1350 ^{0}C. The ultra fast device was a twin rolls, with 1.6-2.75 m/s. By cooling of the melt using twin rolls were obtained glass flakes. Glass flakes were transparent and 1 mm thick. The glass structure was studied by Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DTA) and X-ray diffraction (XRD). The presence of two and more exothermic peaks on DTA curve of glasses indicates the complex crystallization process.

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1. Introduction

Glass can be obtain in BaO-B_2O_3-TiO_2 system by melt and ultra fast quenching technique because their tendency to crystallize [1-5]. Glass ceramics materials can be obtained by controlled thermal treatment of glasses from this ternary system, in which crystallizes BaB_2O_4 [6-8]. Pure B_2O_3 [9] exists in planar three-fold coordination, having an intense absorption. The addition of network modifier ions up to about 15% produces four-fold coordinated boron atoms by cross linking the planar triangle and would be expected to tighten and strengthen the network. The structure of borate glasses is known to be consisting of B – O network, built up from planar three-coordinated and tetrahedral four coordinated boron atoms. Infrared spectroscopy is known to provide insights into the interaction between alkali metal ions and borate glass network. Absorption of these borate glasses is very high in the region of interest of wave numbers bellow 2000 cm^{-1} [10-16].

2. Experimental

Glasses with B_2O_3 bellow 50 mol % were prepared by classical melting at temperature between 1150-1350 ^{0}C for 2 hours. The melt was ultra rapid quenched on a twin rolls device, at 300 rot/min speed. For glass characterization Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DTA) and X-ray diffraction (XRD) were used. FTIR spectra were recorded on a Perkin Elmer SPECTRUM 100 spectrometer, in the range 550-4000 cm^{-1}, using a UATR (Universal Attenuation Total Reflectance) accessory, with a resolution of 8 cm^{-1}, 32 scans and a CO_2/H_2O correction sample ATR contact. For DTA a Mom devices was used heating the samples with 5 and 10^{0}C / min and for XRD a Drone apparatus made the recordings from 5 to 60^o (2θ angle).

The glass oxide compositions, melting temperatures (Tm), speed of the twin rolls, basicity percentage pB and DTA results are presented in table 1.

Table 1. Glass oxide compositions, temperatures of melt, speed of the rolls, pB% and DTA results.

cod sample	BaO mol%	B_2O_3 mol%	TiO_2 mol%	mol% TiO_2/ mol% B_2O_3	Tm ^{o}C	Rolls speed m/s	Tg ^{o}C	pB %	plot
B3	40	50	10	0.2	1210	2.75	552	71.6	1
B6	40	35	25	0.7	1290	1.6	-	71.8	2
B8	40	30	30	1.0	1320	1.6	560	71.9	3
B4	40	25	35	1.4	1350	2.75	561	72.1	4
B1	40	20	40	2.0	1370	2.75	556	72.2	5
B5	45	30	25	0.8	1350	1.6	563	73.9	6
B9	45	25	30	1.2	1380	2.75	596	74.0	7
B2	45	20	35	1.8	1380	1.6	596	74.1	8

The DTA was made to find data about the glasses specific temperatures, Tg (transformation temperature), and crystallization ones. In figure 1 are presented the DTA results for sample 3 recorded with 10 ^{0}C/ min. The Tg is at 552^{o}C and crystallization occurred at 694 and 738^{o}C.

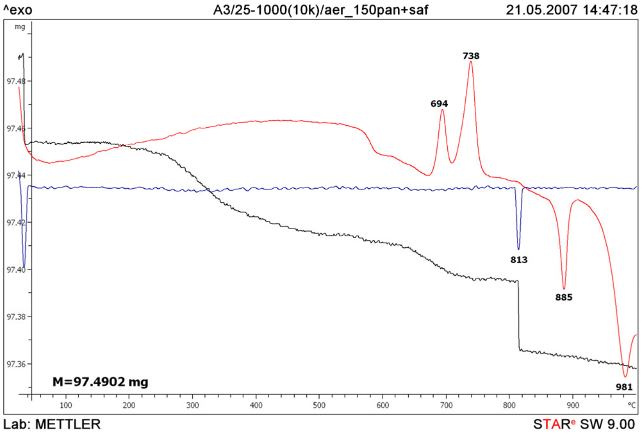

Fig. 1. DTA results for sample B3

The basicity percentage pB [17] was calculated for each composition with the relation (1) and results are given in table 1. It results that, at a constant content of BaO oxide, by increasing the rate mol% TiO_2/ mol% B_2O_3 the basicity percentage pB grows; results are presented in figure 2 (plots are corresponded to oxide composition as noted in table 1)..

$$pB= (44.82*wt\%B_2O_3+89.52*wt\%.BaO+50.67*wt\%TiO_2)/100 \quad (1)$$

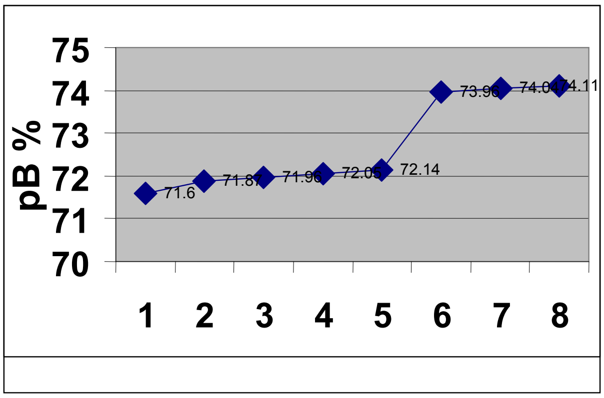

Fig. 2. pB % for glass samples

3. Results

The FTIR spectra gave data about the structure of glasses. Recorded spectra of sample B3, B6, B8, B4 and B1 are presented in figure 3.

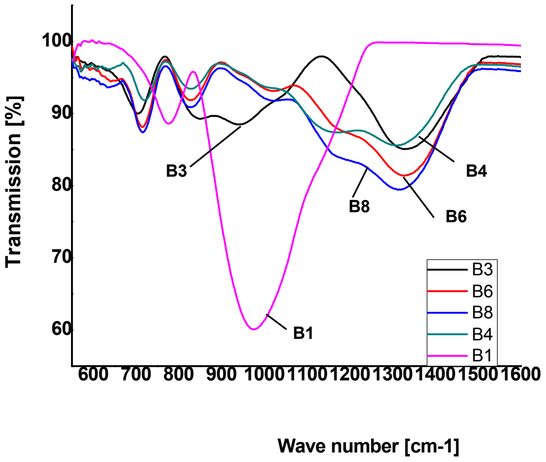

Fig. 3 FTIR spectra of glass samples

There were identified intense bands in the ranges 700-850, 900-1100 and 1150-1450 cm^{-1}. For sample B3 they are centered at 700, 950 and 1350 cm^{-1} (fig 4), and attributed to the vibration of boron atoms with four oxygen atoms surrounding them. XRD analyses showed out that the glass sample after controlled thermal treatment at 800^{0}C for 2 hours became crystallized, with the presence of $BaTi(BO_3)_2$ and BaB_2O_4.

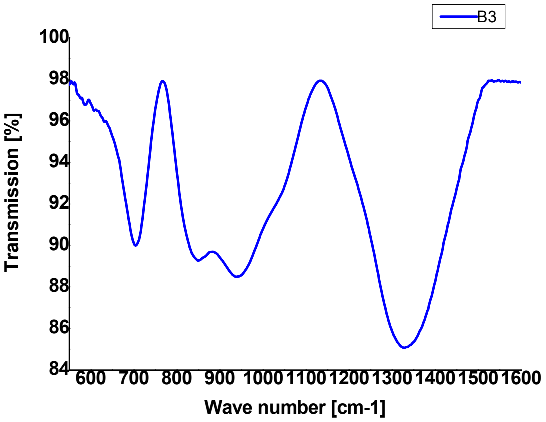

Fig. 4. FTIR spectra of sample B3.

4. Discussion

The bands for BaO are presented at 483 cm^{-1}, intense, and at 503 cm^{-1}, a low one, but for the studied glasses do not appeared, the only vibration band is at ~ 843 cm^{-1} .The bands from ~640 cm^{-1} corresponds to Ti-O vibration. At 790 cm^{-1} were identified the vibration bands for TiO6. The FTIR profile revealed the presence of both BO3 and BO4 units for borate glasses as showed in [20, 21]. In the region 850–1100 cm^{-1}, bands appeared, due to the stretching of B-O bond in tetrahedral BO4 units, which are the vibrations of tetra borate (tri borate and penta borate) groups of BO4 units. Bands from the region 1150–1450 cm^{-1} are attributed to B–O bond stretching of trigonal BO3 units. Between 900 and 1100 cm^{-1} the bands are due to boron atom in tetrahedral coordination, BO4 units. B–O–B bending vibrations are present in the region between 600 and 800 cm^{-1}. Vitreous B_2O_3 presented a lowest absorption band at 720 cm^{-1}, as resulted from figures 3 and 4. The spectra can be divided into the following regions: (1) 700 – 770 cm^{-1} is related to the bending vibrations of various borate arrangements B – O – B, (2) 820 – 1200 cm^{-1} was attributed to the B – O stretching vibrations of tetrahedral BO4 and (3) 1200 – 1400 cm^{-1}, the peaks in this region were related to B – O stretching vibrations of BO3. For sample B3 the FTIR results indicated the presence of B-O stretching vibrations of BO3 units at 1350 cm^{-1} (the biggest value), that can be correlated with the high amount of B_2O_3 (50 mol %).

The glass composition B1 having the smallest amount of B_2O_3 contained BO4 units (at 930 and 1060 cm^{-1}).

As the B_2O_3 content decreases from 50 to 25 mol % the absorption patterns increased from 17 to 20 %.

Table 2. 1. Frequencies and their assignments for IR spectra of BaO -B2O3-TiO_2 glasses.

Wave numbers	Assignment	Ref.
640	Ti-O	[22]
~ 700	B-O-B bending vibrations	[18]
725	Ba – Ti	[16]
~ 770	O_3B-O-BO_4 bending vibrations	[19]
790	TiO6	[22]
~ 825	BO_3-O-BO_3 bonds bending vibration	[19]
843	Ba-O	[23]
~ 930 ~ 1060	B-O stretching vibration of BO_4 units in tri, tetra and penta borate groups	[19]
~ 1160	asymmetric stretching vibration of B-O and / or B-O bonds in borate triangular units (BO3 and BO_2O^-) from pyro- and orthoborate groups	[23]
~1230	B-O stretching vibration of trigonal BO_4 units in boroxol rings	[18]
~ 1370	B-O stretching vibrations of BO3 units in metaborate, pyroborate and ortoborate groups	[15]

The higher absorption is at 40 % for sample B1 having the B_2O_3 = 20 mol %.

The assignments for FTIR results are given in table 2.

DTA results showed out that crystallization occurs in the temperature range 600-800^{0}C. By controlled thermal treatment at 800^{0}C for 2 hours glass ceramic materials were obtained. The Tg values increased as the B_2O_3 content decreased.

In XRD patterns for sample thermal treated at 800 ^{0}C were identified BaTi(BO3)$_2$ and BaB_2O_4 by the following:

BaTi$(BO_3)_2$ 2θ = 30; 23.1; 23; 49.2; 35.8; 43;
BaB_2O_4 2θ = 24.6; 26.9; 14.9; 36.8; 37; 43.2;
BaB_2O_4 2θ =2 5.3; 24.6; 35.7; 44; 14; 29.2

5. Conclusions

Glasses were obtained by melting and ultra fast quenching method in the ternary system having B_2O_3 bellow 50 mol %. To establish the glass structure FTIR and XRD analysis were used. The FTIR results indicated that the BO4 units are the main structural group, due to the most intense bands between 900 and 1100 cm^{-1}.

References

[1] A. Bhargava, J.E. Shelby, R.L. Snyder, J. Non-Cryst. Solids **102**, 136 (1988).
[2] M. Cerchez, L. Boroica, D. Hűlsenberg, Physics and Chemistry of Glasses **41**, 233 (2000)
[3] L. Boroica, E. Rotiu, L. Ionescu, I. Boroica, R. Medianu, 5th Workshop on Nanoscience, Heron Press, Sofia, (2004) 302
[4] L. Boroica, R. Medianu, M. Dinescu I. Boroica, Applied Surface Science **248**, 381 (2005)
[5] A.Bhargava, R. L. Snyder and R. A. Condrate, Sr., Matl. Res. Bull. **22**, 1603 (1987)
[6] L. E. Roțiu, L. Ionescu, I. Boroica, R. Medianu Nanoscience & Nanotechnology'02, Eds. E.Balabanova, I.Dragieva, Heron press, Sofia, (2003), 238
[7] L. Boroica, I. Boroica, E. Roțiu, R. Medianu, D. Hülsenberg SPIE **5581,** 378 (2004).
[8] L. Boroica, I. Boroica, E. Rotiu, B. Sava, R. Medianu D. Hülsenberg 8 th ESG- England 2006 Sunderland, UK 10-14th September 2006, 14
[9] N. Rivier, Phil. Mag. **40**, 859 (1979).
[10] N.S. Abd El-Aal Egypt. J. Solids, **29**, 293 (2006)
[11] A. C. Hannon, R. N. Sinclair, J. A.Blackman, A. C. Wright, F. L. Galeener, J. Non-Cryst. Solids, **106**, 116 (1988).
[12] 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).
[13] P. J. Bray, S. A. Feller, G. E. Jellison Jr., Y. H. Yun, J. Non-Cryst. Solids **38**, 93 (1991).
[14] H. A. Silim J. Solids **29**(2), 293 (2006).
[15] E. I. Kamitsos and G. D. Chryssikos Journal of Molecular Structure **247**, 16 (1991).

[16] J. Javadpour & N. Eror J. Am. Ceram. Soc. **71**, 206 (1988),
[17] P. Balta, C. Spurcaciu, D. Radu, O. Dumitrescu, J. Non-Cryst. Solids **71**, 69 (1985)
[18] I. Ardelean, F. Ciorcas, M. Peteanu, I. Bratu, V. Ioncu, Mod. Phys. Lett. B **14**, 653 (2000).
[19] E. I. Kamitsos, M. A. Karakassides, G. D. Cryssikos, J. Phys. Chem. **91**, 1073 (1987).
[20] Lakshminarayana G, Buddhudu S Spectrochim Acta A Mol Biomol Spectrosc. **62**(1-3), 364 (2005).
[21] Lakshminarayana G, Buddhudu S Spectrochim Acta A Mol Biomol Spectrosc. 63(2), 295 (2006).
[22] C. W. Brown, Rhode Islans, „ Mid-IR and Rama non line spectroscopy, what are the differences” K.D.O Jackson, Internet, J. Vib. Spectrosc., 2, section 3 (1999).
[23] D. de Waal, K.-J. Range, M. Königstein, W. Kiefer, Journal of Raman Spectroscopy, **29**, 109 (1998).

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