J Mater Sci: Mater Med (2007) 18:507–512
DOI 10.1007/s10856-007-2011-3

Structure and dissolution investigation of calcium-bismuth-borate glasses and vitroceramics containing silver

V. Simon · M. Spinu · R. Stefan

Received: 10 August 2005 / Accepted: 4 November 2005

Abstract Quaternary Ag_2O-CaO-Bi_2O_3-B_2O_3 glasses and glassceramics are investigated with regard to release behaviour and local structure. The dissolution behaviour in water and physiological serum shows that the cations are released rapidly or gradually and points out a multi-step process, generally characterised by higher rates in water than in physiological serum. The structural effect of silver addition to bismuth-borate glasses is observed from infrared spectroscopic data. The antibacterial activity of the investigated samples was tested on six bacterial media.

Introduction

Over the past two decades a general experimental and theoretical framework has been developed for understanding the corrosion behaviour of glass in diverse environments [1–3]. Novel systems allowing controlled release of components are intensely investigated [4–6]. Various inorganic antibacterial materials containing silver have been developed and some of them are in commercial use. More chemically durable materials, which slowly release the silver ion for a long period, are developed for medical applications. The silver ions are rapidly released or they can be gradually released into the water at a controlled rate and show an excellent antibacterial property [7]. Silver is capable of killing over 650 different forms of bacteria, viruses, Candida, and molds [8, 9].

Bismuth trace element is used for eye/ear infection and sore throats. The antibacterial activity of bismuth is also known [10, 11]. Although boron is potentially toxic to all organisms, and, as boric acid and borax, has been used as a pesticide and food preservative, higher animals usually do not accumulate boron because of their ability to rapidly excrete it [12]. It appears that boron may influence the production of hormones (including the active form of vitamin D), improve brain and psychological functions, and exert immune-boosting activity [13].

Calcium is essential for all life. It forms part of cell walls and bones. It is important for blood clotting and it is implied in the complicated mechanisms of long-term memory and learning [14, 15].

The composition and local structure at the surface of the samples is of great importance in their dissolution properties. In recent years there has been a considerable increase in the use of the various surface analytical methodologies, including X-ray induced photoelectron spectroscopy (XPS) [16–18]. The XPS technique, in particular, provides information on the first 50–100 Å of the sample surface. Infrared (IR) spectroscopy is a useful tool in characterisation of structural units building glass and vitroceramic materials [19–22].

The aim of this paper is to investigate the dissolution behaviour and the antibacterial effects of quaternary Ag_2O-CaO-Bi_2O_3-B_2O_3 system both for glass and vitroceramic samples in correlation with their microstructure.

Experimental

The investigated samples belong to $xAg_2O \cdot (5\text{-}x)CaO \cdot 10Bi_2O_3 \cdot 85B_2O_3$ system ($1 \leq x \leq 4$ mol%). They were obtained from homogenized mixtures of $AgNO_3$, $CaCO_3$, $Bi(NO_3)_3 \cdot 5H_2O$ and H_3BO_3 chemicals reagents of p.a.

V. Simon (✉)
Babes-Bolyai University, Faculty of Physics, Cluj-Napoca
400084, Romania
e-mail: viosimon@phys.ubbcluj.ro

M. Spinu · R. Stefan
University of Agricultural Sciences and Veterinary Medicine,
Cluj-Napoca 400372, Romania

purity grade by melting at 1050°C for 15 min in sintered corundum crucibles in an electric furnace and quickly undercooling at room temperature by pouring onto stainless steal plates. All as prepared samples were transparent and colourless. For each composition was applied a heat treatment at 575°C for 2 hrs, that leads to a partial crystallisation of samples.

XPS measurements were performed using a PHI 5600ci Multi Technique system. The IR spectra were recorded at room temperature from powdered glass samples pressed in tablets with KBr, in the wave number range 400–4000 $\mathrm{cm^{-1}}$, using a UR-20 Carl Zeiss spectrophotometer with a resolution of 0.6 $\mathrm{cm^{-1}}$ at 1000 $\mathrm{cm^{-1}}$.

The corrosion behaviour was followed in static regime by immersion of disk samples in different solvents (desalinised water, physiological serum and chlorine acid solution with $pH = 1.5$) by measuring the mass of samples maintained in the incubation solutions at 40°C for different times up to 68 hrs. The samples mass was determined by using an analytic balance sensitive to 0.1 mg. The glass surface area to solution volume ratio was around 15 $\mathrm{m^{-1}}$ for all samples. The dissolution rate, DR, was calculated from the measured mass loss Δm (g), samples surface area A ($\mathrm{cm^2}$) and the immersion time t (min) using the equation $DR = \Delta m/(A \cdot t)$ [23].

The sensitivity of different bacteria to the released components was tested in aerobiosis, by use of nutrient agar plates with wells filled with either powdered glass or vitroceramic samples. Streptococcus sp, Bacillus sp, Bacillus anthracis strain R 1190, E. Coli, Salmonella sp. and Pseudomonas pyocyanea were the bacteria inoculated on the agar surface. Diameters of the growth inhibition areas were determined in cm, after 24 hrs incubation at 37°C.

Results and discussion

Some data concerning the releasable cations of the investigated samples, which are of interest with respect to role they could play in oxide glass systems, are summarised in Table 1. The cationic field strength is expressed by the ratio of the cation charge to the square of the ionic radius and is an indication of relative bond strengths. The cations belonging to the conventional glass former oxides are characterised by high field strengths as compared to the cations entering as modifiers. Both calcium and silver ions act as glass network modifiers. One also remarks that Ca^{2+} and Ag^{+} have very close values for ionic radii but they considerably differ with respect to their relative bond strengths. The gradual incorporation of Ag_2O in the calcium-bismuth-borate glasses can be observed from the XPS survey spectra (Fig. 1).

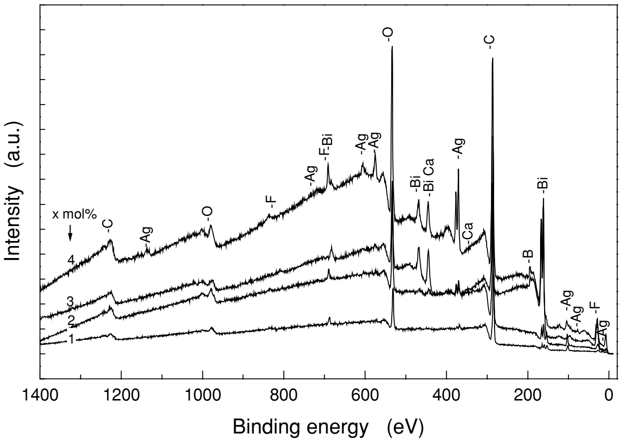

Fig. 1 XPS spectra of $xAg_2O \cdot (5\text{-}x)CaO \cdot 10Bi_2O_3 \cdot 85B_2O_3$ glass samples.

The vitreous B_2O_3 consists of a random network of boroxol rings and BO_3 triangles connected by B-O-B linkages [27]. The addition of other oxides causes a progressive change of the boron coordination from 3 to 4 and results in the formation of various units as diborate, triborate or tetraborate groups [28]. The BO_4 units are connected to form tetraborate units at low modifier content. Vitreous Bi_2O_3 alone cannot be easily obtained, but in multicomponent glass systems the bismuth ions may appear as network formers in [BiO_3] pyramidal and [BiO_6] octahedral units [21, 22, 29, 30].

The IR spectra of the investigated glass samples are given in Fig. 2. Due to the high hygroscopicity of KBr it was difficult to avoid the water adsorption during the grinding

Table 1 Coordination number, ionic radius, field strength, Pauling electronegativity and single bond strength for the cations entering $xAg_2O \cdot (5\text{-}x)CaO \cdot 10Bi_2O_3 \cdot 85B_2O_3$ glasses

Cation	Coordination number	Shannon ionic radius (Å) [24, 25]	Cation field strength ($\mathrm{Å^{-2}}$)	Electro-negativity (Pauling units)	Single bond strength M-O ($\mathrm{kJ \cdot mol^{-1}}$) [26]
B^{3+}	4	0.25	48	2.04	808.8 ± 20.9
	6	0.41	35.69		
Bi^{3+}	6	1.17	2.19	2.02	337.2 ± 12.6
	8	1.31	1.75		
Ca^{2+}	6	1.14	1.53	1.00	402.1 ± 16.7
	8	1.26	1.26		
Ag^{+}	4	1.14	0.77	1.93	220.1 ± 20.9
	6	1.29	0.60		

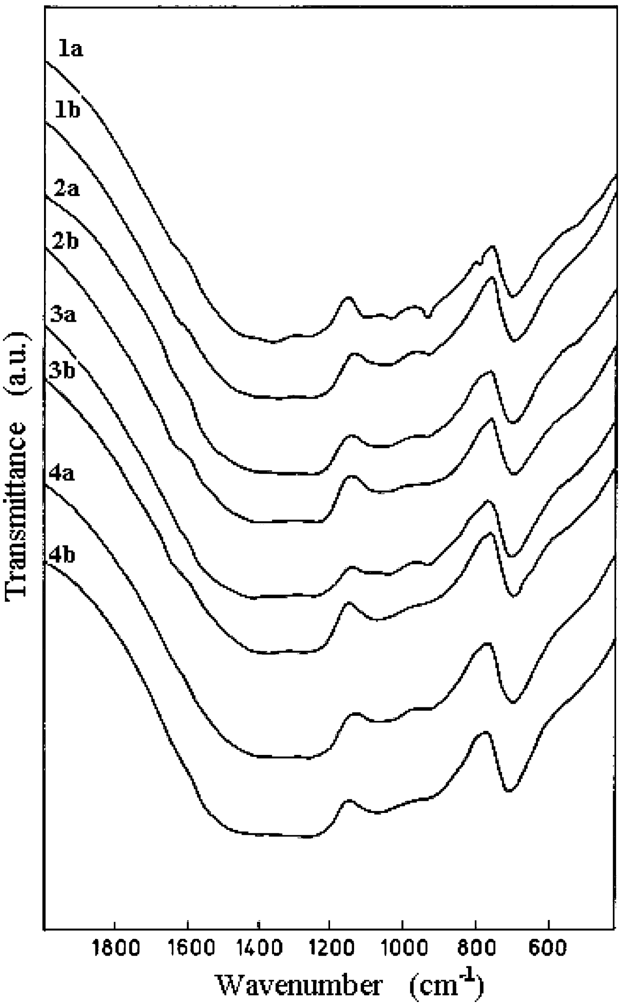

Fig. 2 IR spectra of as prepared (a) and heat treated (b) $xAg_2O \cdot (5\text{-}x)CaO \cdot 10Bi_2O_3 \cdot 85B_2O_3$ glass samples.

of powdered sample in KBr. This leads in the spectral range from 2000 and 4000 cm^{-1} to the occurrence of typical absorption bands ascribed to OH bonds. The position and relative intensity of the minima in the FTIR transmittance spectra can be analysed both as function of silver oxide content and of heat treatment. In the entire spectral range one remarks that the IR spectra for the samples containing 3 and 4 mol% Ag_2O are similar and very weakly influenced by heat treatment. Changes in the microstructure are evidenced both with composition and heat treatment for the samples containing 1 and 2 mol% Ag_2O. The strong band recorded around 700 cm^{-1} is assigned to the B-O-B bending vibrations and the very weak ones appearing around 800 and 1250 cm^{-1} could be attributed to the BO_3 triangular unit vibrations. The BO_4 unit vibrations can be seen in the infrared spectra for all samples between 900 and 1100 cm^{-1} [31, 32]. This result denotes that the change of the boron coordination from BO_4 to BO_3 units is insignificant in the investigated composition range. The weak infrared bands in the 500–670 cm^{-1} spectral range are correlated with the presence of $[BiO_6]$ octahedra [22, 33].

The results of the corrosion test carried out in water and physiological serum are shown in Figs. 3 and 4. The dissolution rate decreases in water from the average value 5 $\mu g/cm^2 \cdot min$ to 0.5 $\mu g/cm^2 \cdot min$ as the Ag_2O content in sample increases from 2 to 4% mol, while in physiological serum the DR values are constant lower, under 1 $\mu g/cm^2 \cdot min$, excepting the sample with 3 mol% Ag_2O for which $DR_{av} = 2.6\ \mu g/cm^2 \cdot min$. Mass losses could not be measured after immersion in HCl solution because all samples softened in the first 15 hrs.

The sensitivity of different bacteria to the released components was evaluated based on the growth inhibition diameters (d) after 24 hrs of incubation. The results obtained after

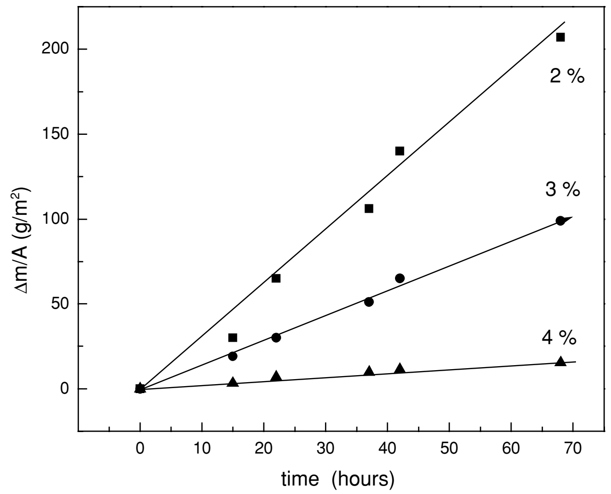

Fig. 3 Time dependence of specific mass loss in water from $xAg_2O \cdot (5\text{-}x)CaO \cdot 10Bi_2O_3 \cdot 85B_2O_3$ glass samples. The lines are only guide for eyes.

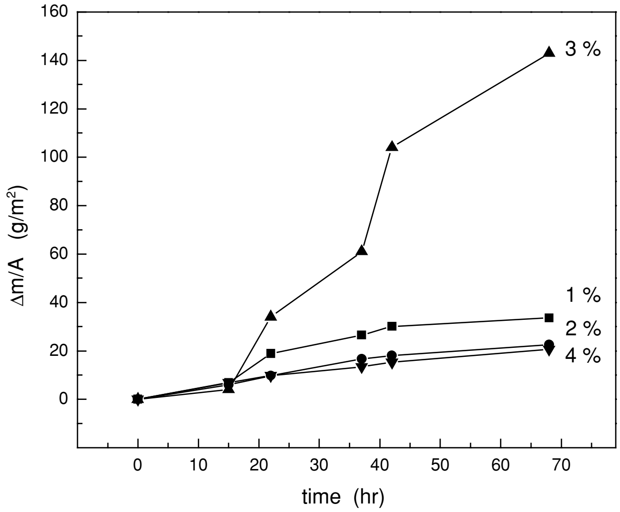

Fig. 4 Time dependence of specific mass loss in physiological serum. The lines are only guide for the eyes.

dissolution of both vitreous and vitroceramic samples are presented in Fig. 5. Bacterial sensitivity depends on silver content, on one hand, but on the sample composition, that is on the local structure, which differs from glass to partially crystallized samples, on the other hand, as well. A more pronounced inhibitory effect is being observed for Gram negative bacteria than for Gram positive ones. A somewhat lower antibacterial activity of the sample containing 4 mol% Ag_2O might be due to the higher dissolution stability of the corresponding glass as showed by corrosion tests.

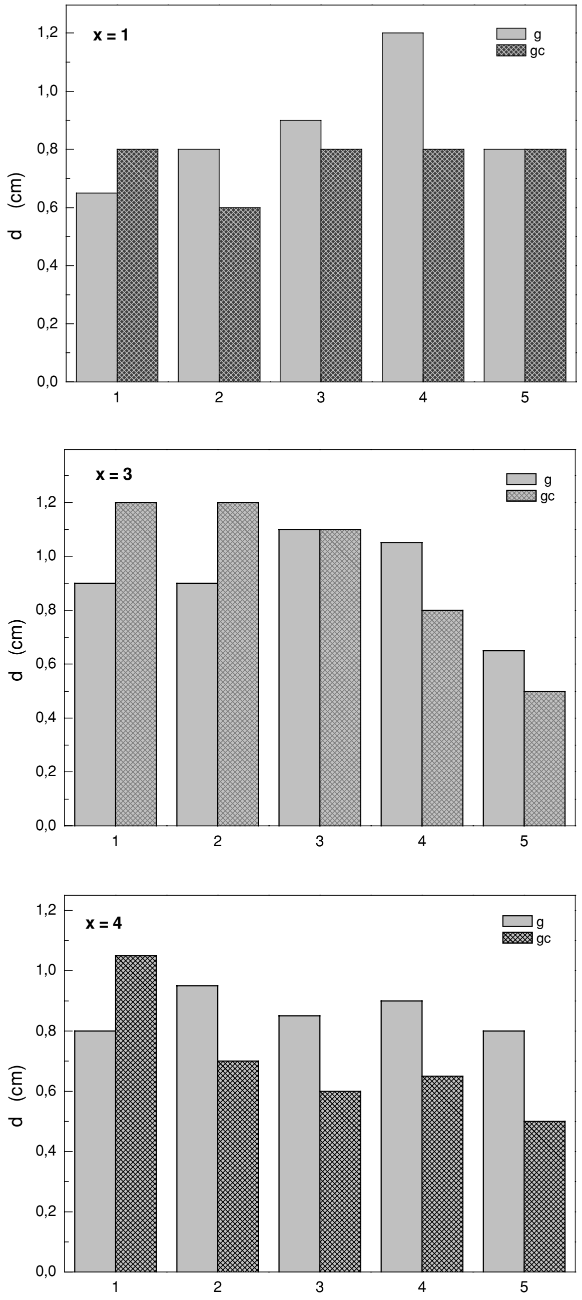

Fig. 5 Inhibitory effect of glass (g) and glassceramic (gc) samples on different bacterial media (1-Bacillus sp.(Antracoid), 2-Bacillus antracis 1190, 3-Salmonella sp., 4-E. Coli, 5-Pseudomonas piocyanea).

In order to explain the different release of cations from the glass network in the investigated dissolution media, beside the composition of glasses and solvents is necessary to take into account the short-range order characterising the samples. The structural stability of cations in glass matrices is correlated with their local symmetry. The local order in glass and crystalline compounds of the same composition has both similarities and differences. The differences are assigned to the loss of long range order, to the deviation from a perfect crystalline structure. The atoms arrangement in the first coordination sphere is determined by the chemical composition and peculiarities of chemical bonds and generates the local order around them, that is very important to depict the vitreous systems. There are also glass systems wherein the local structure is extended at more than some coordination spheres imposing a middle or intermediate range order [34].

The microstructure of $xAg_2O \cdot (5\text{-}x)CaO \cdot 15Bi_2O_3 \cdot 85B_2O_3$ system was earlier investigated by analysing the atomic radial distribution function obtained from X ray scattering data and the correlation with results reported for other similar systems allowed to identify the atom pairs orderly disposed in the investigated samples [35]. They evidenced the occurrence of Ca–B pair as a first coordination formation, well composed at a distance of 1.95–2.0 Å and a rearrangement of these atom pairs as the calcium atoms content decreases in the vitreous system. The distances between Ca–B, B–B and Bi–B pairs are ranging from 2.4 to 2.8 Å and become higher with the silver oxide content from glass samples, while the changes observed for the atoms from the third and forth coordination sphere are very slight. The silver addition to the calcium-bismuth-borate precursor glass preserves the vitreous structure, which evidences the high ability of the precursor glass to accept relatively high Ag_2O content without structural changes. One also noticed a diminution of the atom packing in this system containing silver. The further atoms from the third and forth coordination spheres occur in a less distorted configuration than in the precursor $CaO\text{-}Bi_2O_3\text{-}B_2O_3$ vitreous compound. These results support the differentiated dissolution behaviour of the glass samples with different silver content.

Conclusion

The dissolution behaviour of $xAg_2O \cdot (5\text{-}x)CaO \cdot 15Bi_2O_3 \cdot 85B_2O_3$ vitreous system in water and physiological serum indicates a multi-step process generally characterised by higher rates in water than in physiological serum. The addition of Ag_2O to the lime-bismuth-borate matrix influences the dissolution rate of samples.

The IR results show that the local structure in the investigated samples preponderantly consists of tetracoordinated BO_4 units. BiO_6 structural units were also evidenced. The silver addition to the calcium-bismuth-borate host glass preserves the vitreous structure, evidencing high ability to accept a relatively high Ag_2O content. For the samples containing 3 and 4 mol% Ag_2O the structural units are very weakly influenced by the applied heat treatment. The antibacterial effect of the released cations is more pronounced on Gram-negative bacteria. The magnitude of this effect is in agreement with the cations release rate.

Acknowledgments The authors would like to thank Prof. M. Neumann from the University of Osnabrueck and Dr. I. Bratu from INCDTIM-Cluj for providing access to facilities of their laboratories.

References

1. V. ETTLER, P. BAILLIF and J. C. TOURAY, Natural weathering of glass from Pb-metalurgical slag: a comparison with laboratory leaching tests using XPS. *Bull. Liaison SFMC* **11** (1999) 146–147.
2. T. A. GUITON and C. G. PANTANO, Infrared Reflectance Spectroscopy of Porous Silica Gels and Glasses. *Colloids and Surfaces A* **74** (1993) 33–46.
3. P. J. HAMILTON and C. G. PANTANO, Effects of Glass Structure on the Corrosion Behavior of Sodium-Aluminosilicate Glasses. *J. Non-Cryst. Solids* **222** (1997) 167–174.
4. M. OTSUKA, M. SAWADA, Y. MATSUDA, T. NAKAMURA and T. KOKUBO, Antibiotic delivery system using bioactive bone cement consisting of Bis-GMA/TEGDMA resin and bioactive glass ceramics. *Biomaterials* **18** (1997) 1559–1564.
5. F. DELAHAYE, L. MONTAGNE, G. PALAVIT, J. C. TOURAY and P. BAILLIF, Acid dissolution of sodium-calcium metaphosphate glasses. *J. Non-Cryst. Solids* **242** (1998) 25–32.
6. D. ARCOS, C. V. RAGEL and M. VALLET-REGI, Bioactivity in glass/PMMA composites used as drug delivery system. *Biomaterials* **22** (2001) 701–708.
7. M. KAWASHITA, S. TSUNEYAMA, F. MIYAJI, T. KOKUBO, H. KOZUKA and K. YAMAMOTO, Antibacterial silver-containing silica glass prepared by sol–gel method. *Biomaterials* **21** (2000) 393–398.
8. T. J. BERGER, J. A. SPADARO, S. E. CHAPIN and R. O. BECKER, Electrically generated silver ions: quantitative effects on bacterial and mammalian cells. *Antimicrob. Agents Chemother.* **9** (1976) 357–358.
9. I. MANJUBALA and T. S. SAMPATH KUMAR, Effect of TiO_2-Ag_2O additives on the formation of calcium phosphate based functionally graded bioceramics. *Biomaterials* **21** (2000) 1995–2002.
10. S. L. GORBACH, N. A. CORNICK and M. SILVA, Effect of bismuth subsalicylate on fecal microflora. *Rev. Infect. Dis.* **12** (1990) 21–23.
11. N. A. CORNICK, M. SILVA and S. L. GORBACH, In vitro antibacterial activity of bismuth subsalicylate. *Rev. Infect. Dis.* **12** (1990) 9–10.
12. W. D. LOOMIS and R. W. DURST, Chemistry and biology of boron. *BioFactors* **3** (1992) 229–239.
13. J. G. PENLAND, The importance of boron nutrition for brain and psychological function. *Biol. Trace. Elem. Res.* **66** (1998) 299–317.
14. K. T. BLACKWELL, T. P. VOGL and D. L. ALKON, Cellular mechanisms of calcium elevation involved in long term memory, in *Computational Neuroscience, Trends in Research 1998*, edited by J. BOWER pp. 137–142.
15. K. T. BLACKWELL and D. L. ALKON, Effect of calcium-induced calcium release on associative learning in hermissenda crassicornis. *J. Neurosci.* **24**(Suppl.) (1998) 17.
16. S. AMRAH-BOUALI, C. REY, A. LEBUGLE and D. BERNACHE, Surface modifications of hydroxyapatite ceramics in aqueous media. *Biomaterials* **4** (1994) 269–272.
17. H. ZENG, R. WILLIAM, W. R. LACEFIELD, XPS, EDX and FTIR analysis of pulsed laser deposited calcium phosphate bioceramic coatings: the effects of various process parameters. *Biomaterials* **1** (2000) 23–30.
18. V. SIMON, S. G. CHIUZBAIAN, M. NEUMANN, D. ENIU, E. INDREA, A. TOROK-KISS and S. SIMON, Photoelectron spectroscopy on iron containing CaO-SiO_2-P_2O_5 glass-ceramics. *Mod. Phys. Lett. B* **21** (2000) 767–773.
19. S. G. KAZARIAN, K. L. A. CHAN, V. MAQUET and A. R. BOCCACCINI, Characterisation of bioactive and resorbable polylactide/Bioglass® composites by FTIR spectroscopic imaging. *Biomaterials* **18** (2004) 3931–3938.
20. A. COSTANTINI, R. FRESA, A. BURI and F. BRANDA, Effect of the substitution of Y_2O_3 for CaO on the bioactivity of $2.5CaO \cdot 2SiO_2$ glass. *Biomaterials* **6** (1997) 453–458.
21. L. BAIA, R. STEFAN, W. KIEFER, J. POPP and S. SIMON, Structural investigations of copper doped B_2O_3-Bi_2O_3 glasses with high bismuth oxide content. *J. Non-Cryst. Solids* **303** (2002) 379–386.
22. L. BAIA, R. STEFAN, J. POPP, S. SIMON and W. KIEFER, Vibrational investigations of highly iron doped B_2O_3-Bi_2O_3 glass systems. *J. Non-Cryst. Solids* **324** (2003) 109–117.
23. M. KARABULUT, E. MELNIK, R. STEFAN, G. K. MARASINGHE, C. S. RAY, C. R. KURKJIAN and D. E. DAY, Mechanical and structural properties of phosphate glasses. *J. Non-Cryst. Solids* **288** (2001) 8–17.
24. R. D. SHANNON, Revised effective ionic radii in halides and chalcogenides. *Acta Cryst.* **A32** (1976) 751–767.
25. J. E. HUHEEY, E. A. KEITER and R. L. KEITER, in "Inorganic Chemistry: Principles of Structure and Reactivity" (HarperCollins, New York, USA, 1993) 4th edn.
26. J. A. KERR, in "CRC Handbook of Chemistry and Physics," edited by D. R. LIDE (CRC Press, Boca Raton, Florida, USA, 2000) 81-st ed.
27. J. KROGH-MOE, The structure of vitreous and liquid boron oxide. *J. Non-Cryst. Solids* **1** (1969) 269–284.
28. R. L. MOZZI and B. E. WARREN, The structure of vitreous boron oxide. *J. Appl. Crystallogr.* **3** (1970) 251–257.
29. S. HAZRA and A. GHOSH, Structure and properties of nonconventional glasses in the binary bismuth cuprate system. *Phys. Rev. B* **51** (1995) 851–856.
30. S. HAZRA, S. MANDAL and A. GHOSH, Properties of unconventional lithium bismuthate glasses. *Phys. Rev. B* **56** (1997) 8021–8025.
31. W. C. HUANG, H. JAIN, E. I. KAMITSOS and A. P. PATSIS, Anomalous expansion of sodium triborate melt and its effect on glass properties. *J. Non-Cryst. Solids* **162** (1993) 107–117.
32. E. I. KAMITSOS, J. A. KAPOUTSIS, G. D. CHRYSSIKOS, J. M. HUTCHINSON, A. J. PAPPIN, M. D. INGRAM and J A DUFFY, Infrared study of AgI containing superionic glasses. *Phys. Chem. Glasses* **36** (1995) 141–149.

33. A. A. KHARLAMOV, R. M. ALMEIDA and J. HEO, Vibrational spectra and structure of heavy metal oxide glasses. *J. Non-Cryst. Solids* **202** (1996) 233–240.

34. R. E. YOUNGMAN, S. T. HAUBRICH, J. W. ZWANZIGER, M. T. JANICKE and B. F. CHMELKA, Short- and Intermediate-Range Structural Ordering in Glassy Boron Oxide. *Science* **269** (1995) 1416–1420.

35. R. STEFAN, V. SIMON and E. INDREA, Structural characterization of silver containing bismuth-borate glasses by X-ray scattering. *Int. J. Mod. Phys. B* **17** (2003) 3857–3865.