PROPRIETĂȚI ALE STICLELOR DIN SISTEMUL $BaO - B_2O_3 - TiO_2$
PROPERTIES OF GLASSES FROM $BaO - B_2O_3 - TiO_2$ SYSTEM

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By controlled crystallization of glass samples from $BaO - B_2O_3 - TiO_2$ system glass ceramics can be obtained, based on borates and barium titanate (β – BaB_2O_4 and $BaTiO_3$), with potential uses in electronics and electrical engineering. In this paper are presented the obtaining and some properties of glasses from the ternary system $BaO - B_2O_3 - TiO_2$, containing B_2O_3 between 20 and 50 molar%. For the obtained samples were determined density, thermal expansion coefficient, micro hardness, viscosity and hydrolytic stability. Determinations were also made by differential thermal analysis (DTA). The variation of the determined properties according to the oxide glass composition was explained.

Prin cristalizarea controlată a probelor de sticlă din sistemul $BaO - B_2O_3 - TiO_2$ se pot obține vitroceramici pe bază de borați şi titanați de bariu (β – BaB_2O_4 şi $BaTiO_3$), cu potențiale utilizări în electronică şi electrotehnică. În această lucrare sunt prezentate modul de obținere precum şi o serie de proprietăți ale sticlelor din sistemul ternar $BaO - B_2O_3 - TiO_2$, cu un conținut de B_2O_3 cuprins între 20 şi 50 % molare. Pentru sticlele obținute au fost determinate densitatea, coeficientul de dilatare termică, microduritatea, vâscozitatea şi stabilitatea hidrolitică. Totodată s-au făcut determinări de analiză termică diferențială (ATD). Modul de variație al proprietăților determinate s-a explicat în funcție de compoziția oxidică a sticlelor.

Keywords: *borate glasses, DTA, dilatometry, chemical properties*

1. Introduction

Recent research has lead to the establishment of new uses of vitreous and ceramic materials, such as photovoltaic materials as thin films used in solar cells to convert light into electricity, optical and electrical switches, memory, ultra-transparent optical fiber used in telecommunications, protective coatings for machine tools and components, decorative coatings, active elements and flat TV playback devices [1-3]. Further development of electronic industry requires the use of new materials with special properties more accessible by developing new materials research and development of various methods of production. These materials must have default electrical and dielectric properties, must present a good chemical stability and capacity of welding metallic, ceramic or vitreous materials. Vitreous materials can be made relatively easily in different sizes and shapes: block, sheet or fiber and oxide composition can be easily changed to obtain established properties [4]. Glasses can be used in a broad technical background in electronics, like sensors, flat panel displays, micro-analysis systems, micro-actuators and implants [5].

The first research carried out in the system $BaO-B_2O_3-TiO_2$, is communicated by Bargava A. and Pernice P. [6-9]. In 2000 the first results were presented in the TiO_2-rich domain, in which was obtained by controlled crystallization barium titanate [10]. In 2006 were studied by Feitosa et al. [11] glass compositions $x_1BaO-x_2B_2O_3-x_3TiO_2$, where x_3 = 4, 8, 15 mol. % and x_1/x_2 = 8/9. By controlled crystallization, were obtained partially crystallized materials from the surface, were identified crystals β-BaB_2O_4 (β - BBO) and/or $BaTi(BO_3)_2$. Glasses from the ternary system $BaO-B_2O_3-TiO_2$, containing large amount of TiO_2 (20-40% molar) were studied to develop nonlinear optical materials [12]. In the system $BaO-B_2O_3-TiO_2$, nanoscale ceramic powders were obtained containing β - BaB_2O_4 [13] and TiO_2 in the proportion of 4, 8 and 16% molar. The obtained materials were used for making thin films by different physical methods of submission. Glasses of $BaO-ZnO-B_2O_3$ system (BZB) [14] showed a dielectric constant of 14-18 and a thermal expansion coefficient of 8.9 × 10-6 / K.

This paper studies the route to obtain and some properties of glasses in the ternary system $BaO- B_2O_3-TiO_2$, containing B_2O_3 between 20 and

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50 molar%. These glasses can easily lead to obtaining glass ceramics with electronic applications. The second part of the paper will clarify the structure of glass and some dielectric characteristics. A correlation with the structure and properties of the dielectric composition will be made.

2. Experimental

Glass compositions containing boron oxide between 20-50 molar% were studied. Oxide composition of the studied glasses is presented in Table 1. Reagents p.a. grade (ICD Romania $BaCO_3$, TiO_2 and B_2O_3 ICD Fluka-Germany Romania) were used. Quantities of 100 g of raw materials were realized, dry homogenized, and then melted in a platinum crucible at temperatures between 1100 and 1200 ^{0}C, for 2 hours. Melts were cooled by pouring between metal plates. Glass blocks were annealed at 540 to 550 ^{0}C for 1 hour.

Table 1

Oxide compositions and the melting temperature for the glasses from the BaO - B_2O_3 - TiO_2 system
Compozițiile oxidice studiate şi temperatura de topire pentru sticlele din sistemul BaO - B_2O_3 - TiO_2

Sample code *Cod probă*	Composition *Compoziție*			Melting temperature *Temperatura de topire*
	BaO mol %	B_2O_3 mol %	TiO_2 mol %	^{o}C
B1	40	20	40	1200
B3	40	50	10	1100
B13	35	30	35	1200
B14	30	40	30	1200
B15	25	50	25	1100

For the obtained glasses were determined: density by hydrostatic method using a Shimadzu balance [15] with a kit for hydrostatic density and thermal expansion coefficient (α), measured with a Linseis L75 dilatometer. Using differential thermal analysis (ATD) curves were recorded for 0.3-0.5 mm grain powders using a MOM Q 1500D device type, in the temperature range of 20 to 1000 ^{0}C and glass transition temperature TG was measured.

Thermal expansion coefficient was measured according to [16-17], by using dilatometer method, with a single glass rod 3x3x15 mm size. The measurement was performed between 25 and 575 ^{0}C. Micro hardness glass was determined by Vickers method [18-19], using a device ПМТ-3. Experiments were performed with the use of 50, 80 and 100 g loads, with indentation duration of 20 sec. For the obtained indentation the diagonally is measured and the value of micro hardness calculated.

Vickers micro hardness calculating formula was [18]:

$$Hv=1.854 \times P / d^2 \ (N/m^2) \qquad (1)$$

Where: P is the indenter load in kg;
d is the average diagonals, in m.

Optical Digital Microscope with Motic software IMAGE PLUS 2.0 was used to visualize the Vickers indentation mark. Glasses viscosity variation with temperature [20] was established using the penetrometer (ISO 7884-1) for the viscosity domain: $\eta = 10^8 - 10^{12}$ dPa·s [21]. Hydrolytic stability was determined using the conductometric method, using 1 g of glass powder of 0.3-0.5 mm size, placed in 50 ml of distilled water. Conductance was measured for 250 min. ISO 719 only tests the water capability to extract water soluble basic oxides [22-23].

3. Results and discussion

The results of measurements of density, temperature of vitreous transition TG and linear thermal expansion coefficient α are shown in Table 2. Density decreases with B_2O_3 increasing and BaO and TiO_2 content decreasing. However it is acceptable that TG decreases as the TiO_2/B_2O_3 ratio decreases respectively B_2O_3 content increases at the expense of BaO and TiO_2.

Linear thermal expansion curve for sample B13, having the closest composition to equimolarity, is shown in Figure 1. The ordinates are the sample length variation (Delta L) and linear thermal expansion coefficient (Alpha-tech) for the temperature range between 25 and 575 °C. The thermal expansion coefficient α is 10.8×10^{-6} / K, low annealing temperature, Tir, is 496.2 ^{0}C, TG is 535.8 ^{0}C, high annealing temperature, TSR, is

Table 2

Values of density, temperature of vitreous transition TG, α - coefficient of thermal expansion for the studied glasses, reported to TiO_2/B_2O_3 / *Valorile pentru densitate, temperatura tranziției vitroase Tg şi coeficient de dilatare termică α, pentru sticlele studiate, funcție de raportul TiO_2/B_2O_3*

Sample code *Cod probă*	TiO_2/B_2O_3 % mol	Density/ Densitate g/cm^3	Tir ^{0}C	TG ^{0}C	Tsr ^{0}C	α 10^{-6} /K
B1	2.0	4.3836	494.1	532	544.6	11.0
B13	1.16	4.2971	496.2	535.8	547.7	10.8
B14	0.75	4.1244	485.3	525	537.6	10.6
B15	0.5	4.0299	481.7	520	533.5	10.5
B3	0.2	3.8488	502	552	564.2	10.4

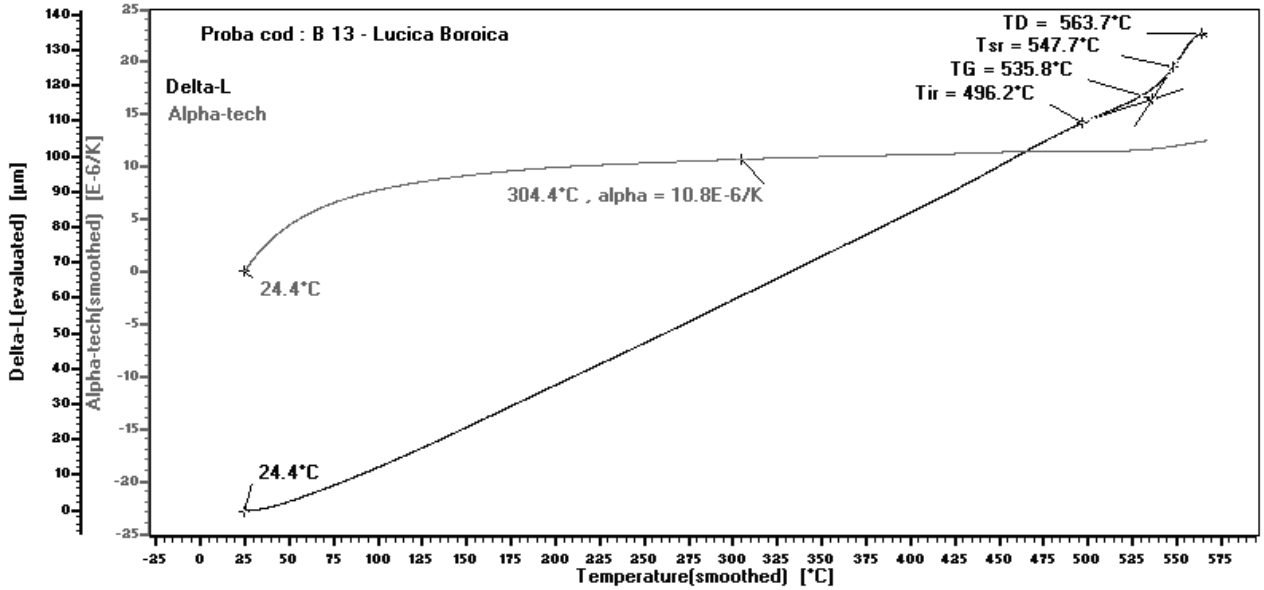


Fig. 1 - Linear thermal expansion curve for sample B13. The lower curve shows the variation ordered sample length and upper curve linear thermal expansion coefficient / *Curba de dilatare termică lineară pentru proba B13. Pe ordonată curba inferioară prezintă variația lungimii probei, iar curba superioară coeficientul de dilatare termică lineară.*

547.7 ^{0}C and TD is 563.7 ^{0}C. Values of α has a slightly downward trend as the ratio R = TiO_2/B_2O_3 and BaO % decrease, as observed in Table 2. The explanation is that at low values for R and BaO %, B_2O_3 structure becomes dominant, the BO bonds are in priority to the Ti-O or Ba-O type, which have significantly higher coefficients of expansion.

Differential thermal analysis (DTA) for the extreme samples, from point of the view of the titanium oxide and boron oxide content, the rate of those tow oxide respectively, showed high tendency to crystallization for sample B1, with the lowest content of B_2O_3, the highest ratio TiO_2/B_2O_3 (2) and highest BaO content (40% mol). Figures 2 and 3 present recorded DTA curves with a heating rate of 10 ^{0} C/min for B1 and B3 samples, respectively, with the same content of BaO. Composition B3 has the lowest ratio R = TiO_2/B_2O_3= 0.2 and the lowest content of TiO_2 (with oxide composition BaO = 40 molar %, B_2O_3 = 50 molar % and TiO_2 = 10 molar %). Note that for sample B1 due to the large amount of TiO_2 present in the composition the Tcr1 crystallization peak from 688 ^{0}C is very high. B3 sample showed the lowest crystallization peaks at 689 ^{0}C and 739 ^{0}C, respectively. The exothermic from 688-689 ^{0}C may be attributed to crystallization of the ternary compound $BaTi(BO_3)_2$.

The B13 sample presented crystallization effects less pronounced then sample B1, but more

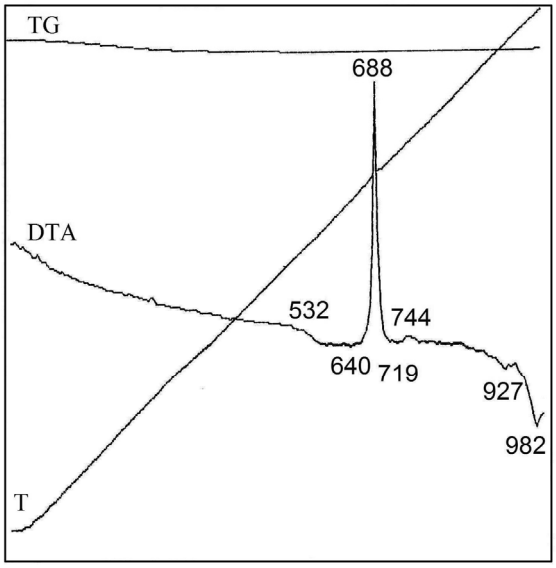


Fig. 2 - DTA results for sample B1 cooled on metal plate, analyzed with a heating rate of 10 °C/min. / *Rezultatele ATD pentru proba B1 răcită pe placa metalică, analizată cu viteza de încălzire de 10 °C/min.*

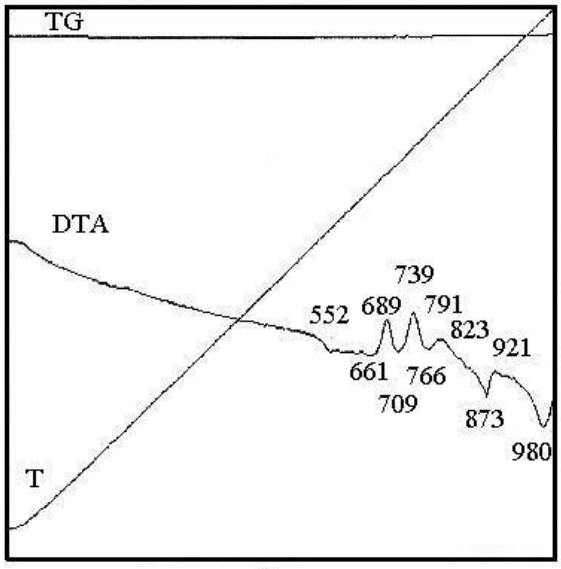


Fig. 3 - DTA results for sample B3 cooled on metal plate, analyzed with a heating rate of 10 °C / min./ *Rezultatele ATD pentru proba B3 răcită pe placa metalică, analizată cu viteza de încălzire de 10 °C / min.*

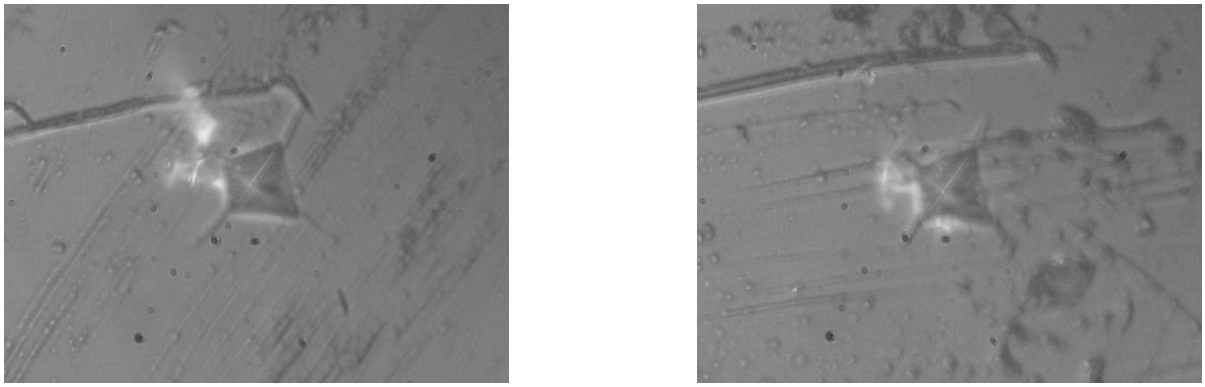


Fig. 4. a) Vickers imprint for sample *B1/ Amprenta Vickers pentru proba B1.*

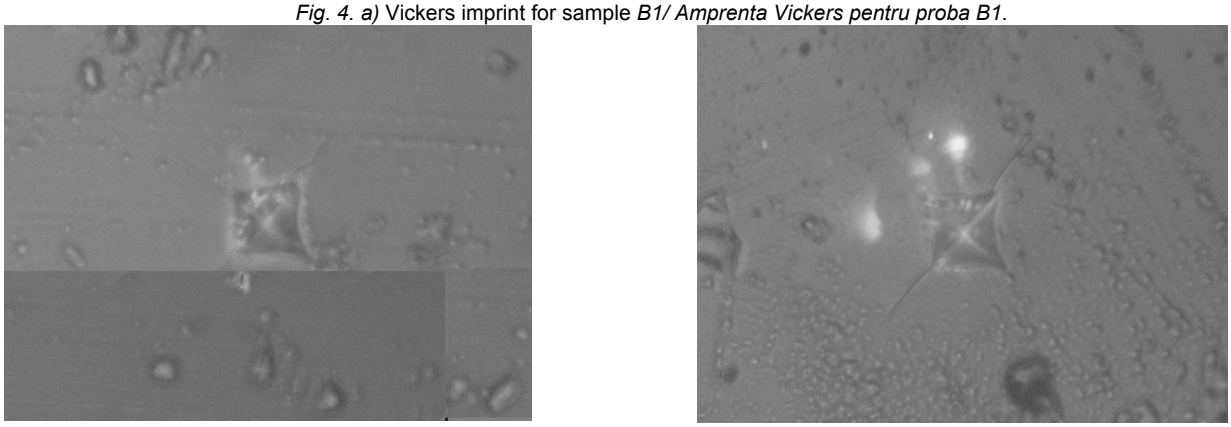


Fig. 4. b) Vickers imprint for sample *B3/ Amprenta Vickers pentru proba B3.*

intense then sample B14 and B15, which showed reduce crystallization effects, resembling with sample B3. The exo and endothermic effects were evidenced, in the case of these samples, at temperatures closer to those presented in Figures 2 and 3 for the extremes, B1 and B3.

Imprint images for samples B1 and B3 indents, visualized with optical microscopy Motic digital kit are shown in Figures 4a and 4b.

We notice the presence of cracks in three corners of the imprint, for sample B1 and only in two opposite corners for B3 glass. MHV values are slightly higher for sample B3. Cracks appeared in print corners can give information on the so called "degree of corruption" [19]. If one considers the influence of glass former oxides, which show increased cracking resistance for increased boron concentration, in this case B3 sample has a higher content of B_2O_3 than B1.

The results of micro-hardness measurements for the extreme samples B1 and B3, chosen as representative, are presented in Table 3. Graphical representation of Figure 5 shows that, although the curves slopes are different micro-hardness value is very close for indentation mass of 80 g.

Table 3.

Vickers indentation results for samples B1 and B3/ *Rezultatele indentărilor Vikers pentru probele B1, şi B3*

Sample B1 obtained by cooling on metal plate *Proba B1 obținută prin răcire pe placă*					Sample B3 obtained by cooling on metal plate *Proba B3 obținută prin răcire pe placă*				
Weight *Greutate* g	d Div	D (medium / *mediu*) Div	mm	Micro hardness *Microduritate* daN/ / mm^2	Weight *Greutate* g	d Div	D (medium/*mediu*) Div	mm	Micro hardness *Microduritate* daN/ / mm^2
50 50 50 50	46 42 49 47	46	13.8	478	50 50 50 50	47 42 49 42	45	13.5	499
80 80 80 80	59.5 52.5 53.5 57.5	54.75	16.42	540	80 80 80 80	57 52 57 54	55	16.5	535
100 100 100 100	57.5 63 62 60.5	60.75	18.22	547	100 100 100 100	50 55 62 60	56.75	17.0	628

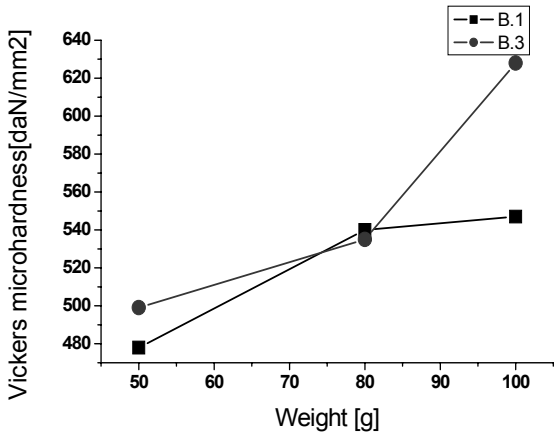
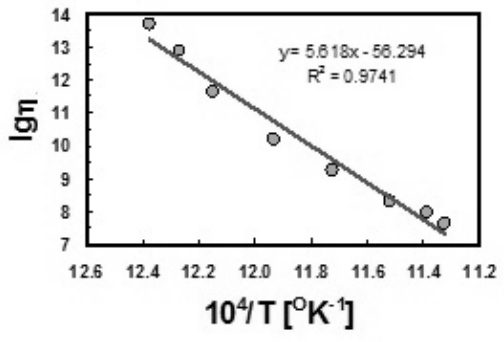


Fig. 5 - Vickers micro hardness for samples B1 and B3 *Microduritatea Vickers pentru probele B1 şi B3.*

If you make a comparison with the MHV for soda-lime-silicate glass, which is about 454 daN/mm^2 [24] in the case of B1 and B3 studied glasses the values are slightly higher for a load of 100 g.

Glass viscosity, η, is the most important property in the process of conditioning and shaping, strongly influencing the conditions of melting, refining and flow [25-29]. Viscosity - temperature curve was determined using the penetrometer-viscometer in 10^7 - 10^{14} dPa.s domain (between 530 and 620 ^{0}C).



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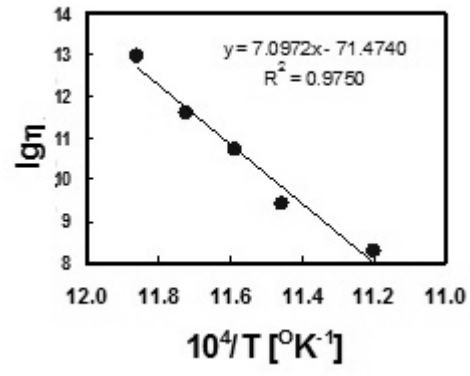

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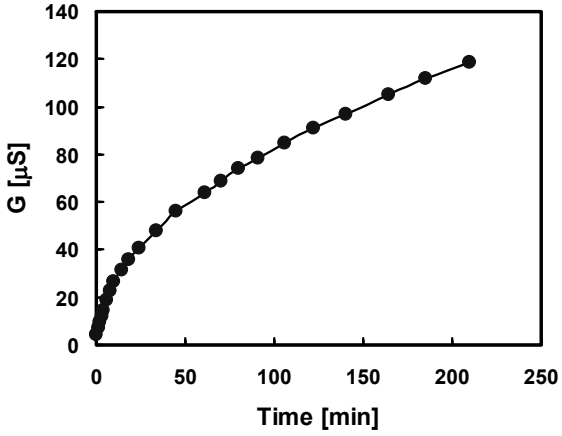
Fig. 6 - Lg η to 10^4/T representation for glass sample a) B13 and b) B15 / *Reprezentarea lg η funcție de 10^4/T pentru probele de sticlă a) B13 şi b) B15.*



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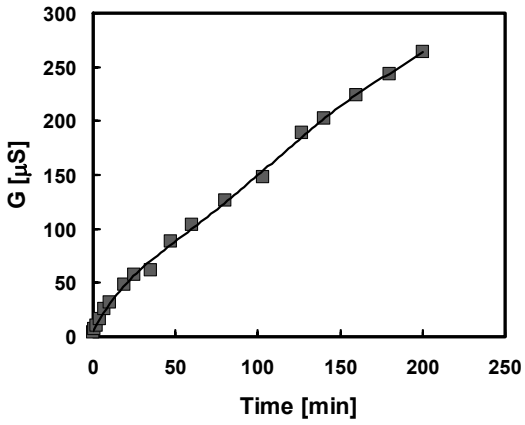

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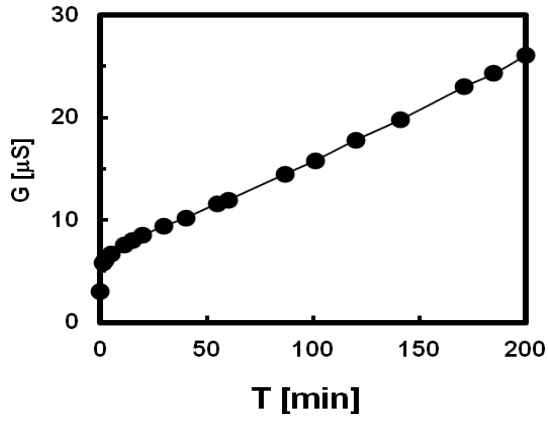

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Fig. 7 - Hydrolytic stability of: a) sample B13, b) sample B15 and sample soda - lime, measured by conductivity method / *Stabilitatea hidrolitică a: a) probei B13 b) probei B15 şi c) proba sticla silico calco-sodică, măsurată prin metoda conductometrică.*

The results of viscosity measurements for B13 and B15 glass samples are presented in Figure 6.

Curves of variation of viscosity with temperature have similar slopes for the two

analyzed samples. Compared with usual industrial glasses (soda-lime-silicate, boro-silicate, etc.) from these curves is observed that for the studied glasses the working domain is short, having a variation for viscosity of 4.6 - 5 orders in 50 - 75 ^{0}C.

It was observed that increasing B_2O_3 content leads to increased working domain by 25 ^{0}C. If we compare the two glasses is observed that lg η is 11.6 for the temperature of 550 respectively 580 ^{0}C. Hydrolytic stability measurement results are presented in Figure 7 a) and b) for B13 and B15 glasses. Note that hydrolytic stability is low compared to values measured under the same conditions for a soda-lime- silicate glass (only up to 45 μS sample c), reaching, for B15 sample the level of about 260 μS.

4. Conclusions

They obtained five blocks of glass with different chemical compositions in the BaO - B_2O_3 - TiO_2 system by melting and cooling on metal plate. Were determined a number of physical properties of glasses and the results were correlated with their chemical composition.

It was observed that the density decreases with increasing of the B_2O_3 amount and decreasing of BaO and TiO_2 content. Vitreous transition temperature is within a relatively tight variation, between 520 and 552 ^{0}C for all studied samples.

For 80 g indentation mass, Vickers micro-hardness value was very close for samples having the smallest and respective the biggest B_2O_3, concentration B1 and B3 , 540 respectively 535 daN/mm^2 .

The studied glasses showed a low working domain, with a viscosity variation of 4.6 - 5 magnitude orders within 50 to 75 ^{0}C interval.

Hydrolytic stability for these glasses is low compared to values measured under the same conditions for soda-lime-silicate glass.

REFERENCES

1. M. Cerchez, L. Boroica and G. Constantinescu, New applications of sintered glasses, Building Materials, 1992, **XXII**, 304.
2. I. Boroica, M. Cerchez and L. Boroica, Glasses with high thermal expansion coefficient and increased durability, for sealing with several metals and alloys, Proceedings of Vth International Conference Joining Ceramics, Glass and Metal, Jena, Ed. German Society of Glass Technology, 1997, 116.
3. C. Spurcaciu, E. Balta, M. Cerchez and L. Boroica, Glass for pasivating of silicium crystal in the B_2O_3- SiO_2- ZnO system, The XIXth Tehnico - Scientifically Meeting, Medias, Romania, 1988.
4. D. Hulsenberg, Micro and nanostructured glasses, Synthesis and processing of nanostructured materials, Ceramic engineering and science proceedings, Cocoa Beach, 2008, **27**, 8.
5. Y. Zuo-Guang, Handbook of Advanced Dielectric Piezoelectric and Ferroelectric Materials: Synthesis, Properties and Applications, Woodhead Publishing Ltd, 2008, 109.
6. A. Bhargava, R.L. Snyder and R.A. Condrate, Sr., Preparation of $BaTiO_3$ glass-ceramics in the system Ba-Ti-B-O, Materials Letters, 1988, **7** (5-6), 185.
7. A. Bhargava, R.L. Snyder and R.A. Condrate, Sr., The Raman and infrared spectra of the glasses in the system BaO-TiO_2-B_2O_3, Materials Research Bulletin, 1987, **22** (12) 1603.
8. A. Bhargava J.E. Shelby and R.L. Snyder, Crystallization of glasses in the system BaO-TiO_2-B_2O_3, J. Non-Cryst. Solids, 1988, **102**, 136.
9. P. Pernice, S. Esposito and A. Aronne, Structure and nonisothermal crystallization of glasses in the BaO–B_2O_3–TiO_2 system, Phys. Chem. of Glasses, 1998, **39** (4), 222.
10. M. Cerchez, L. Boroica and D. Hulsenberg, Glasses and crystallized glasses in BaO-B_2O_3-TiO_2 system, Phys. Chem. Glasses, 2000, **41**,233.
11. C.A.C. Feitosa, V.R. Mastelaro, A.R. Zanatta, A.C. Hernandes and E.D. Zanotto, Crystallization, texture and second-harmonic generation in TiO_2–BaO–B_2O_3 glasses, Optical Materials, 2006, 28 (8-9), 935.
12. S. Kosaka, Y. Benino, T. Fujiwara, V. Dimitrov and T. Komatsu, Synthesis and nonlinear optical properties of $BaTi(BO_3)_2$ and $Ba_3Ti_3O_6(BO_3)_2$ crystals in glasses with high TiO_2 contents, J. of Solid State Chemistry, 2005, **178**, 2067.
13. L.J.Q. Maia, M.I.B. Bernardi, A.R. Zanatta, A.C. Hernandes and V.R. Mastelaro, β-BaB_2O_4 nanometric powder obtained from the ternary BaO–B_2O_3–TiO_2 system using the polymeric precursor method, Materials Science and Engineering, 2004, **B107**, 33.
14. S–G. Kim, H. Shin, J–S. Patk, K.S. Hong and H. Kim, Effect of SiO_2 Addition to BaO-ZnO-B_2O_3 Glass on Dielectric and Thermal Properties for Application to Barrier Ribs of Plasma Display Panels, Journal of Electroceramics, 2005, **15**, 129.
15. A. Fluegel, Global Model for Calculating Room-Temperature Glass Density from the Composition, J. Amer. Ceram. Soc., 2007, **90** (8), 2622.
16. xxx, ISO 7991-1987.
17. xxx, ASTM C372-94: 2001.
18. xxx, ASTM C730-98- 1998.
19. P. Baltă, Glass technology, Didactical and Pedagogical Publishing House, 1984, 144.
20. xxx, ASTM C1350M-96: 2003.
21. xxx, ISO 7884-1: 1998-02.
22. xxx, ISO 719-1985.
23 D.B. Rapp and J.E. Shelby, Water diffusion and solubility in soda-lime-silica melts, Phys. Chem. Glasses, 2003, **44** (6), 393.
24. G. With and H.H.M. Wagemans, Ball-on-Ring Test Revisited, J. Am. Ceram. Soc. 1989, **72**, 1538.
25. R. Năstase and A. Volceanov, Method for viscosity measurement, with multi functional apparatus, – Romanian patent, Romanian Journal of Materials, 2008, **38** (2), 104.
26. C. Căpățână and P. Baltă, Rubin copper glass- new data and interpretationa, Romanian Journal of Materials, 2003, **33** (1) 18.
27. P. Baltă and C. Căpățână, Factors influencing the redox processes implicating Cu in oxide glasses, Romanian Journal of Materials, 2003, **33** (2), 94.
28. D. Radu, M.S. Nicolescu and S. Radicescu, Prrercentual evaluation offragility degree of vitrogen melts, Romanian Journal of Materials, 2007, **37** (1), 17.
29. P. Baltă, New experimental method for glass structure study, Romanian Journal of Materials, 2008, **38** (4), 315.

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