U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 2, 2011 ISSN 1454-2331

LASSES OBTAINING FROM BOROSILICATE GLASS CULLET AND COPPER CONTAINING SLUDGE

Luminița Daniela URSU[1], Adriana DIACONU[2], Bogdan Alexandru SAVA[3], Adrian VOLCEANOV[4]

Lucrarea prezintă un studiu al deşeurilor înglobate în sticlă (cioburi de sticlă borosilicatică şi nămol care conține metale grele, în principal cupru) pentru obținerea sticlelor colorate decorative. Sunt investigate proprietățile sticlelor obținute: coeficientul de dilatare termică şi temperaturile caracteristice din dilatograme, transmisia optică în vizibil şi infraroşu apropiat, stabilitatea hidrolitică, unghiul de umectare şi vâscozitatea. Utilizarea deşeurilor conduce la economii de materii prime, necesare pentru obținerea sticlelor.

The paper presents a study of the industrial waste incorporating in glass (the borosilicate glass cullet and sludge that contain heavy metals, mainly copper) in order to obtain decorative colored glasses. The samples properties such as thermal expansion coefficient and characteristic temperatures obtained from thermal expansion diagrams, UV-VIS-NIR transmission, hydrolytic stability, wetting angle and viscosity are investigated. Waste reusing in glass leads to reduction of raw materials amount in glass obtaining.

Keywords: decorative glass, borosilicate cullet, copper containing sludge

1. Introduction

In Romania the dangerous waste represents an important environmental pollution source due to the fact that their storage and stocking are often improperly [1]. The paper takes into account the national policy for dangerous waste management by developing a technology for neutralizing the dangerous waste with metal content and the adoption of the Comunitary acquis in the field of waste management / dangerous waste [2-4].

The paper presents a study of the industrial waste (borosilicate glass cullets and sludge that contain heavy metals) ment to obtain decorative colored glasses for external decorations (decorative glass, slabs for interior or exterior plating of buildings). These technologies could contribute to the preservation of

[1]Scientific Researcher III, National Institute of Glass, Bucharest, Romania, e-mail: danielaursu2004@yahoo.com
[2] Scientific Researcher I, National Institute of Glass, Bucharest, Romania
[3] Scientific Researcher I, National Institute of Glass, Bucharest, Romania
[4] Prof., Depart. of Oxide Materials Science & Engineering and Nanomaterials, University POLITEHNICA of Bucharest, Romania

natural raw materials which could be replaced by recovered metal compounds as raw materials and/or pigments for glass.

Another way to reuse the borosilicate glass cullet, with certain compositions is to obtain various glass resistant to high temperature and pressure, products called transparent level gauge glasses and disc sight glasses [5]. Materials like glass are ideal to include toxic substances due to their stability, because they present minimum risks to spread dangerous waste in the environment.

The vitrifying process requires to monitor and correct the chemical structures of fusions before and after vitrification and to rigorously control the final products features, which are stable for a long time and usage.

Generally, for including the dangerous waste in a vitreous matrix the following manufacturing parameters should be taken into consideration: elaboration temperature, viscosity and homogeneity of melted glass, components volatility at elaboration temperature, furnace refractory corrosion etc.

2. Experimental part

The borosilicate glass cullets (having thermal expansion coefficient in the range of 3.3÷5 x 10^{-6}°C^{-1}), come from pharmaceutical industry (white glass ampoules D1 and brown glass ampoules D3) and laboratory equipments industry [6], components for the apparata in the chemical industry and equipments for temperature and density measurement (laboratory glass D2).

The chemical composition of the borosilicate glass waste, D1, D2 and D3 is presented in Table 1.

Table 1

Weight gravimetric composition of the borosilicate glass waste

Waste// Composition (weight %)	SiO_2	Al_2O_3	Fe_2O_3	CaO	B_2O_3	Na_2O	K_2O	BaO	TiO_2
Waste from white glass ampoules D1	73.58	5.1	0.048	1.71	11.60	6.50	1.08	0.36	-
Waste from laboratory glass D2	79.88	2.40	-	0.3	13.02	3.87	0.33	0.2	-
Waste from brown glass ampoules D3	71.32	5.12	0.68	1.23	11.06	5.75	1.14	1.30	2.40

The source of the sludge containing heavy metals (iron, copper, zinc, cadmium, chromium, nickel, etc.), is represented by dangerous waste resulting from ferrous metallurgy and metal industries, waste incineration, waste water treatment plants. The chemical composition of the sludge widely varies and depends on the process that takes place in the manufacturing line and the purification technology used by each company [7,8]. The influence of the sludge containing copper is discussed in the paper.

The industrial waste (the sludge with copper) is aqueous sludge, which is dried and milled. Drying takes place in a furnace with 200 dm^3 capacity, at 120°C for 4 hours. The dried sludge is then milled in a planetary mill for 2 hours. The planetary mill contains four agate bodies and agate balls. The resulting powder has the grains size under 100 μm. The chemical composition of the sludge containing copper is presented in Table 2.

Table 2

Chemical analysis of copper sludge

Cu	Zn	Cr	Ni	Pb	Mn	Other elements (OH^- & CO_3^{2-})
51.68	0.79	0.03	0.01	0.39	0.07	47.03

Table 3 presents the raw materials used for glass samples with borosilicate glass cullet and sludge containing copper. The code of glass recipes is RB5.1.x.y where „5” represents the precursory recipe, „1” represents the quantity of sludge with copper, “x” number is the type of borosilicate glass waste added (D1- white glass ampoules, D2- laboratory glass and D3- brown glass ampoules) and “y” number represents the quantity of borosilicate glass waste.

Table 3

Raw materials recipes for glass samples RB5.1.

Raw materials (weight, g)	RB 5.1.0.0	RB 5.1.1.15	RB 5.1.1.30	RB 5.1.1.43	RB 5.1.2.15	RB 5.1.2.30	RB 5.1.3.15	RB 5.1.3.30	RB 5.1.3.45
Sand	154.0	142.9	131.9	154.0	142.0	130.0	143.3	132.6	154.0
Soda	76.2	76.2	76.2	76.2	76.2	76.2	76.2	76.2	76.2
Potassium	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5
Boric acid	8.9	5.8	2.7	0.1	5.4	2.0	6.0	3.0	0.1
Cryolite	8.5	7.5	6.5	5.6	8	7.5	7.5	6.5	5.5
Zinc oxide	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1	32.1
Copper	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Waste (D1, D2, D3)	0	15	30	43	15	30	15	30	45

The oxide compositions weight (%) calculated for RB5.1.x.y glass samples are presented in table 4.

Table 4

Oxide weight compositions of glasses containing borosilicate waste and sludge with copper

Composition (wt %)	RB 5.1.0.0	RB 5.1.1.15	RB 5.1.1.30	RB 5.1.1.43	RB 5.1.2.15	RB 5.1.2.30	RB 5.1.3.15	RB 5.1.3.30	RB 5.1.3.45
SiO_2	61.48	61.15	60.73	64.78	61.30	61.11	60.99	60.53	64.51
CaO	-	0.10	0.20	0.26	0.02	0.04	0.07	0.15	0.19
BaO	-	0.02	0.04	0.05	0.01	0.02	0.08	0.15	0.20
Na_2O	19.45	19.57	19.64	17.53	19.54	19.62	19.46	19.48	17.33
K_2O	3.13	3.18	3.22	2.89	3.14	3.15	3.17	3.21	2.89
Al_2O_3	0.82	0.93	1.23	1.24	0.92	1.01	1.03	1.22	1.26
B_2O_3	2.00	1.99	1.97	1.76	1.99	2.00	1.99	1.97	1.74
ZnO	12.81	12.75	12.66	11.20	12.78	12.74	12.71	12.62	11.13
Fe_2O_3	-	-	0.01	0.01	-	-	0.04	0.08	0.11
CuO	0.31	0.31	0.31	0.27	0.31	0.31	0.31	0.30	0.27
TiO_2	-	-	-	-	-	-	0.14	0.28	0.37
$\sum$	100	100	100	100	100	100	100	100	100

Experimental melting processes were conducted according to the chemical compositions presented in table 4. The raw materials were crushed using an agate mojar and sieved on a 0.2 mm sieve. A 0.5 mm sieve was used for cullet sieving. The quality of the glass depends on the raw materials and the quality of the mixture preparation. The mixture was homogenized for 20 minutes. Thermal treatments take place in a high–temperature electrical laboratory furnace, equipped with superkanthal elements. Refractory crucibles with a capacity between 0.5 *l* and 1.2 *l* were used. Melting diagram for RB5.1 series is presented in Fig. 1.

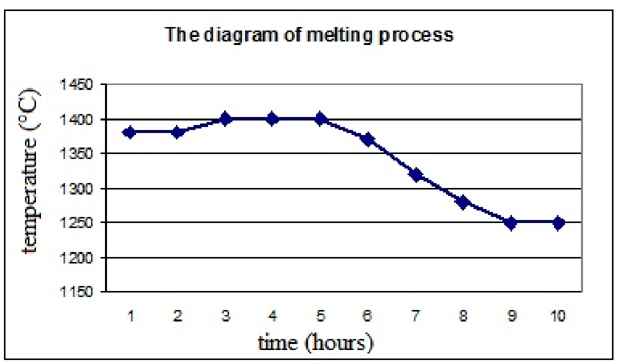


Fig 1. Melting diagram for RB5.1 series, in electric furnace

The mixture of raw materials, borosilicate cullets and sludge containing copper was melted at 1380ºC. Temperature was increased with 20°C for the refining process, and it was maintained at this level for 2 hours. The melted glass cooling was conducted, from 1380ºC to 1250°C, in 4 hours, average cooling speed beeing around 30°C/hour.

The glass was casted into a pre-heated form made from refractory steel, with 60x60x20mm dimensions. Fig. 2 presents the annealing treatment diagrame for RB5.1 series.

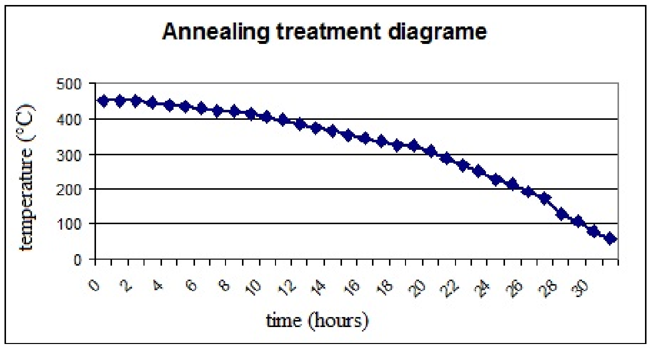


Fig 2. Annealing treatment diagram for RB5.1 series

Some properties such as: linear coefficient of thermal expansion with the characteristic temperatures dilatometric temperature (TD), superior annealing temperature (Tsr), vitrous transition temperature (TG) and inferior annealing temperature (Tir) from thermal expansion diagrams, hydrolitic stability, wetting capacity and viscosity are investigated for the RB5.1.x.y glasses.

The thermal expansion coefficient and the critical temperatures were measured by LINSEIS L72 dilatometer. The parameters were: measurement range: 0-1000^{o}C; air; increasing temperature rate: 1-30 degree/min; quartz piston; accuracy: ±1μm for the length variation (Δl); $\pm 10^{-7}$ / $^{\circ}$C measurement error for the expansion coefficient; PC system with recording and electronic processing of the expansion curve, expansion coefficient, characteristic temperatures of the glass.

Optical transmissivity in visible and near infrared region of spectra were measured by CINTRA 202 spectrometer using CINTRAL software*,* with technical parameters: Wavelength Range (1150.01–190.008 nm); Scan Speed (1000 nm/min); Step Size (0.426667 nm); Slit Width (1.5 nm); D2 Lamp (Automatically changed at 350 nm); Beam Mode (Double).

The glass viscosity was measured using a penetometer - vyscosimeter equipped with cylindrical penetration body. The glass viscosity was measured in the range 10^{8}-10^{13} dPas. The method uses the following devices: an electrical furnace with kanthal wire in which the sample is heated, the penetometer (made from hard materials, such as nitrides or carbides) that applies the force and measures the depth of penetration. The depth curve as a function of time is plotted for several temperatures.

The ability of sealing the different materials such as ceramics or metals was analyzed by measuring the wetting angle. An optical microscope RD 200, Russia with an electric furnace was used, equipped with kanthal wire. The support was a ceramic material and the glass sample dimensions were 4 × 4 × 4 mm. The optical measurements were made down to the wetting angle of 90^o.

Hydrolytic stability was determined by conductometry. This method involves the measure of electric conductance variation for glass powder suspension in accordance with time. The same temperature, glass powder quantity with specific surface and suspension concentation are maintained. The experiments were done at constant temperature (25°C), glass powder granulation (between 0.22 and 0.32mm), glass powder quantity (1g) and water amount (50 ml), The glasses stability is presented in a comparative way and the same grafic representation of hydrolytic stability for more glasses since it is a qualitative method.

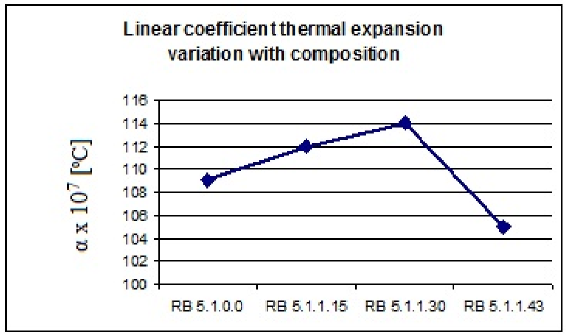
3. Results and discussions

The thermal expansion coefficients and the characteristic temperatures for these glasses are presented in table 5. Based on these data, we plotted the diagram for the variation of the thermal expansion coefficients related to the composition for the RB5.1 series (Fig. 3). Volatilities during the melting process have an influence on the final weight gravimetric composition of the glass and on the thermal expansion coefficient. A small variation of the thermal expansion coefficient with the increasing amount of cullets that replaced the raw materials was established. The amount of sludge containing copper was maintained constant for all the samples.

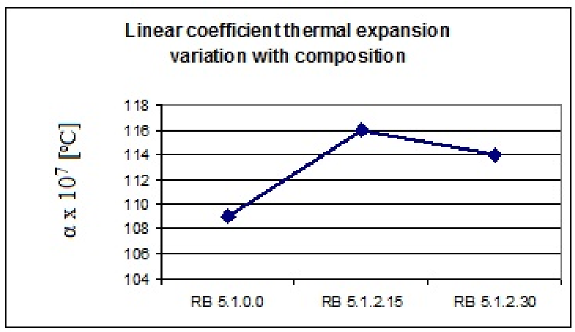
Table 5

Thermal expansion coefficients and characteristic temperatures for the RB 5.1 series

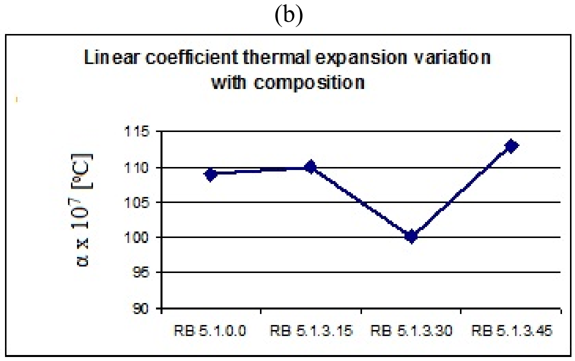
Sample code	Thermal expansion coefficients (α) $[°C^{-1}]x10^7$	TD [ºC]	Tsr [ºC]	TG [ºC]	Tir [ºC]
RB 5.1.0.0	109	498.8	466.8	457.1	433
RB 5.1.1.15	112	497.1	470.6	462.5	446.2
RB 5.1.1.30	114	490.7	466.6	455.5	427.2
RB 5.1.1.43	105	510.9	484.4	472.3	440.5
RB 5.1.2.15	116	490.8	464.5	453.6	428.7
RB 5.1.2.30	114	499.9	475.5	462.5	435.6
RB 5.1.3.15	110	510.7	482.8	470.7	450.8
RB 5.1.3.30	100	522.2	492.7	480	454.1
RB 5.1.3.45	113	508.3	478.2	468.1	449.8



(a)



(b)

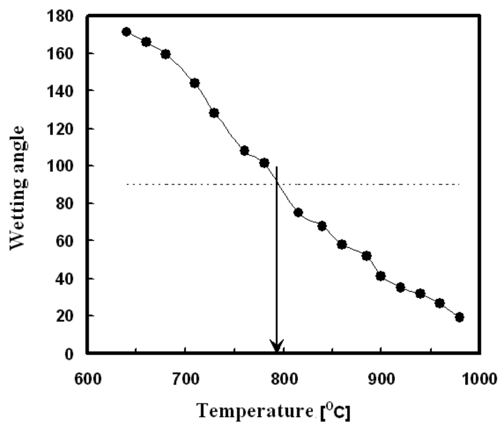


(c)

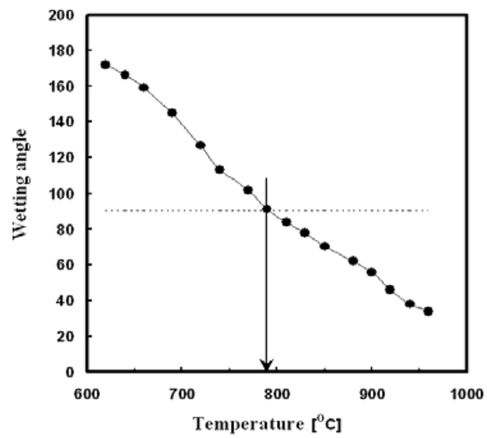
Fig 3. Linear coefficient variation chart of the of thermal expansion for RB 5.1 series (a) waste from white glass ampoules D1; (b) waste from producing laboratory glass D2 and (c) waste from brown glass ampoules D3

The experimental data concerning wetting angle-temperature dependence for RB 5.1.2.15, RB 5.1.2.30 and RB 5.1.3.30 glasses are presented in Fig. 4. Measurements were done at a constant heating rate of the furnace (4ºC/min).

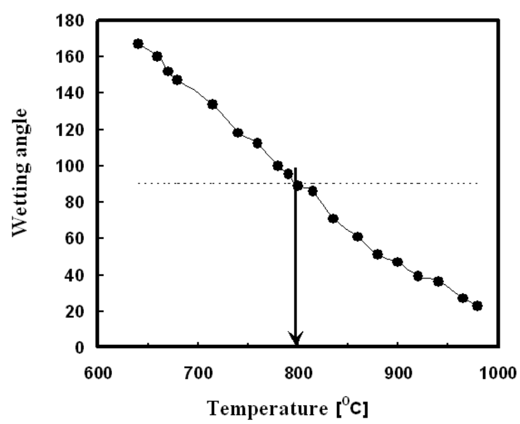
The viscosity - temperature dependance for **RB 5.1.2.15, RB 5.1.2.30** and **RB 5.1.3.30** glasses was studied in 10^8 – 10^{13} dPa.s domain. Experimental data were correlated with mathematical relations such as Arrhenius and Vogel, Fulcher, Tamman (VFT).



(a)



(b)



(c)

Fig 4. Wetting angle-temperature dependance for RB 5.1.2.15 (a), RB 5.1.2.30 (b) and RB 5.1.3.30 (c) (the dashed line at 90˚ represents the overcross from the non wetting to wetting domain)

All studied glasses were analyzed with Arrhenius and Vogel, Fulcher, Tamman methods for **RB 5.1.2.15, RB 5.1.2.30 şi RB 5.1.3.30** (Fig. 5). The correlation coefficient $\mathbf{R^2}$obtained for VFT relation is higher than that obtained with Arrhenius relation (0.9926>0.9464, 0.9814>0.9788 and 0.9874>0.9701). Viscosity - temperature dependence may be as VFT type for these glasses. More experimental data are required for a better assessment of viscosity - temperature dependence in a larger domain of viscosity (at $10^2 – 10^3$ dPas up to 10^{13} dPa.s).

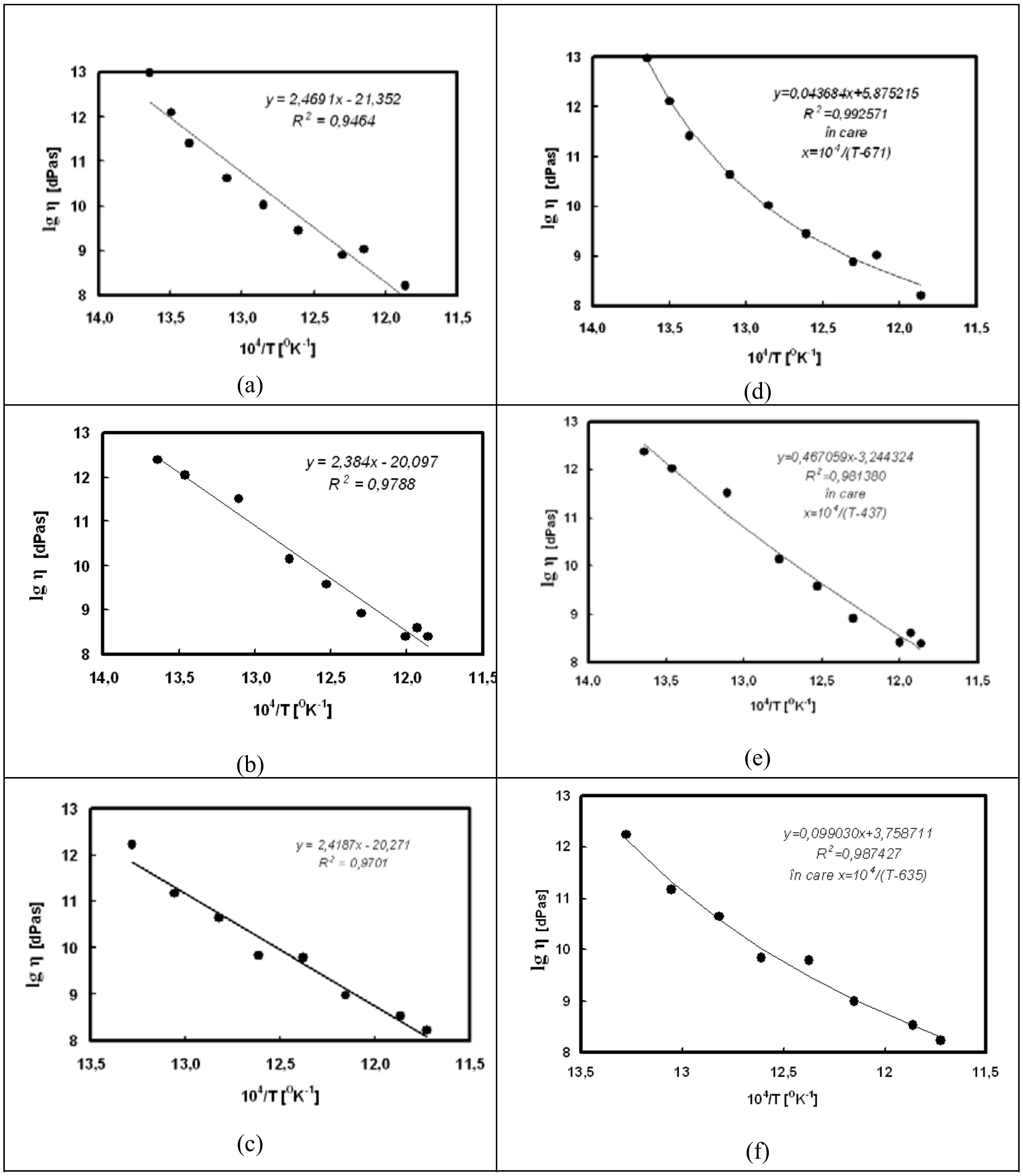


Fig 5. Viscosity - temperature dependance for RB 5.1 series: experimental data correlated with Arrhenius relationship: (a) for RB 5.1.2.15 glass, (b) for RB 5.1.2.30 glass and (c) for RB 5.1.3.30 glass; experimental data correlated with VFT relationship: (d) for RB 5.1.2.15 glass, (e) for RB 5.1.2.30 glass and (f) for RB 5.1.3.30 glass

The experimental data regarding glass powder hydrolitic stability are plotted in Fig. 6 were glass conductivity against time is given for the studied samples. The temperature, glass powder quantity, specific area and suspension concentration are maintained constant.

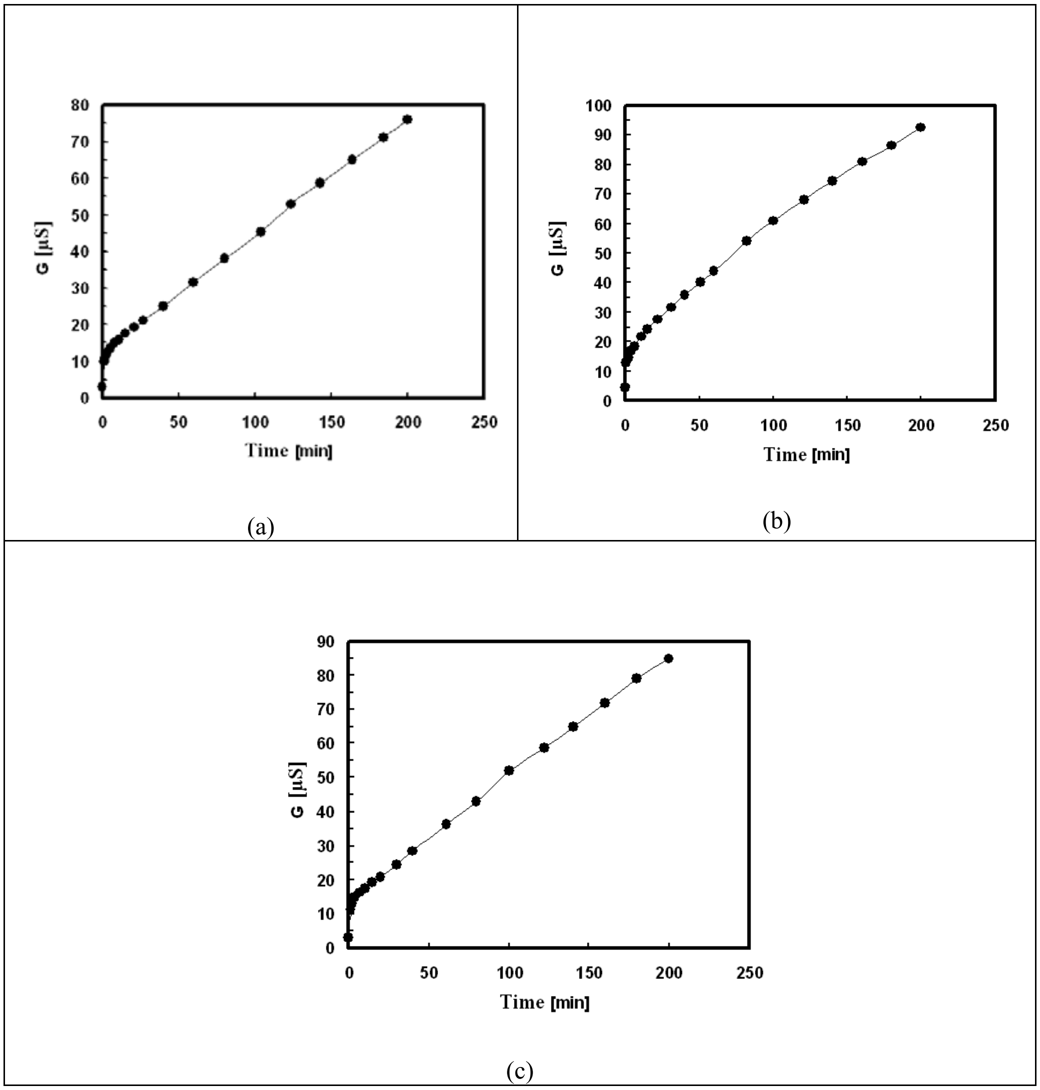


Fig 6. The dependence of glass powder suspension in water
for RB 5.1.2.15 (a) glass, RB 5.1.2.30 (b) glass and RB 5.1.3.30 (c) glass

From the variation of the conductance on time for RB 5.1.2.15, RB 5.1.2.30 and RB 5.1.3.30 glasses, it can be observed that RB 5.1.2.15 glass is the most stable because its conductance variation is the lowest at the same measuring time (200 min).

The experimental data concerning transmission spectra are presented in Figs. 7 – 9.

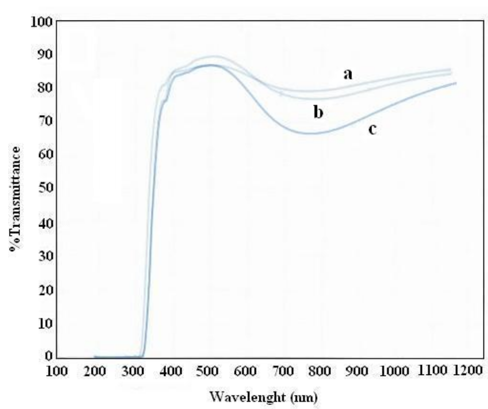


Fig 7. Transmission spectra for RB 5.1.1.15 (a) glass, RB 5.1.1.30 (b) glass and RB 5.1.1.43 (c) glass

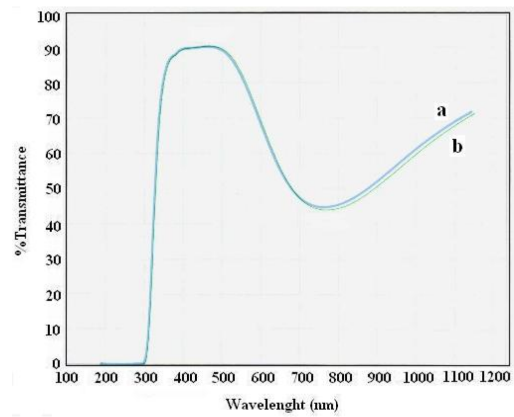


Fig 8. Transmission spectra for RB 5.1.2.15 (a) glass and RB 5.1.2.30 (b) glass

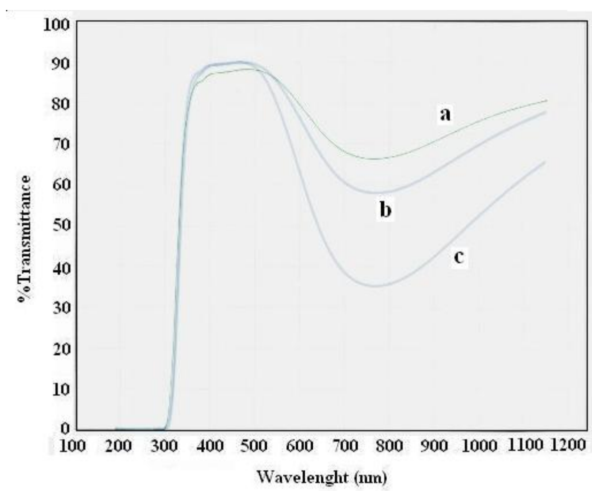


Fig 9. Transmission spectra for RB 5.1.3.15 (a) glass, RB 5.1.3.30 (b) glass and RB 5.1.3.45 (c) glass

In glasses doped with copper, three different oxidation states of copper are possible. The most common is the Cu^{2+} which is the origin of the (greenish) blue color of the respective glasses. Under normal (oxidizing) conditions, Cu^{2+} is in equilibrium with Cu^+, which is colourless [9]. Under reducing conditions, the formation of colloidal Cu^0 particles is possible, which can lead to a red colour of the glass samples (so called "copper ruby glasses").

The blue color of the glass samples can be explained in terms of the transmission spectra, which show maximum transmittance in the range 460–510 nm. Visible absorption spectra of these decorative colored glasses have revealed two absorption bands at around (460-510 nm) and (760-780 nm), both attributed to Cu^{2+} ions absorption [10].

The absorption bands observed for transition metal ion doped silica matrix are due to the electronic transitions of the 3*d* electrons of the ion. When the transition metal ions are coordinated with other ions, the energy levels of these *d* electrons are split by the electric field of the coordinating ions instead of being degenerated as in the free ions.

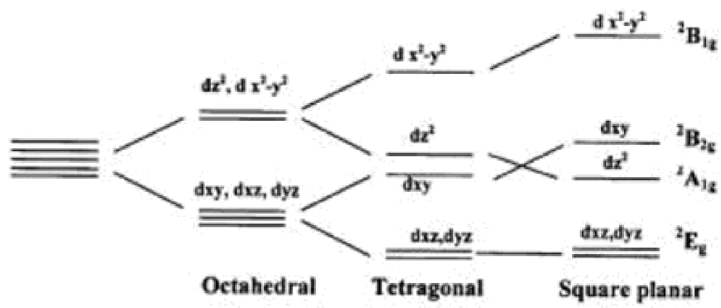


Fig 10. Energy level diagram for d^9 Cu^{2+} free ion in octahedral, tetragonal and square planar coordination

It is known that the diluted Cu^{2+} ions inside glass matrix exhibit a broad optical absorption band around 780 nm, assigned to the 2*E*g–2*B*1g transition (Fig. 10) due to Jahn–Teller splitting of *d* levels of Cu^{2+} ions in a ligand field. There are three possible *d*–*d* electronic absorption transitions, corresponding to 2*E*g–2*B*1g, 2*A*1g–2*B*1g and 2*B*2g–2*B*1g [11].

The absorption increases with borosilicate waste content from 15 to 45%, in series RB 5.1. Another explanation of the absorption increase in the case of RB 5.1.3.45 sample is the increase of iron content to 0.11 wt %.

4. Conclusions

The borosilicate waste can be recuperated from various compositions glass with no significant influence over the physical and chemical properties of decorative glasses, comparatively with glasses without such waste.

The chemical composition of the sludge with copper depends on the processes that take place in the product line, and on the purification technology used by each economic agent. The used sludge has a high content in one metal (for this case, copper), and a low content in other types of metals. Because the sum of all heavy metals is over 3%, the sludge is considered a dangerous waste. It can not be stored; it has to be processed/stabilized before storage. So, these dangerous types of waste (borosilicate cullet and copper sludge) are included in a vitreous matrix in order to obtain decorative colored glasses.

Cu^{2+} ions embedded in glass matrix lead to important absorption of light, mostly in 760-780 nm area, for all obtained glasses. For these wavelengths the light transmission decreases within 20% and 60%, respectively, in the case of 15 and 45% borosilicate waste containing glasses.

The advantages of using borosilicate glass waste and recuperated copper from sludge are reusing valuable components in the recipes (B_2O_3, CaO, Al_2O_3, cromophore oxides), saving the raw materials, energy and ecological environment.

R E F E R E N C E S

[1] *O. Dumitrescu, V. Dima, D. Radu, M. Eftimie, A. Diaconu, L.D. Ursu,* " Sticle realizate cu deşeuri vitroase şi nămoluri cu nichel", Revista Română de Materiale, 39(3), 2009, pp. 217-225

[2] Directive 2006/12/EC of the European parliament and of the council on waste, 5 April 2006

[3] "Council Directive 91/689/EEC on hazardous waste", Official Journal L 377, 31 December 1991, pp. 20-27

[4] "Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste", Official Journal L 182, 16/07/1999 P. 0001 – 0019

[5] *A. Diaconu, L.D. Ursu, B.A. Sava, D. Radu, I. Mitiu, E. Rosu* "Evaluation of reusing borosilicate glass cullet for manufacturing glass resistant to high temperature and pressure", CEEX Conference 2008, Brasov, 27-29.07.2008, published in "Excellence Research – a way to innovation", **vol. II**, Editura Tehnica, Brasov, 2008, pp 204.1-204.6, ISSN 1844-7090

[6] *A. Diaconu, B.A. Sava, L.D. Ursu, D. Paraschivescu, C. Radulescu, D. Radu, O. Dumitrescu, V. Dima, M. Eftimie, I. Mâtiu, E. Rosu, C. Necula, G. Stefanescu,* "Quality and quantity evaluation for borosilicate glasses waste, generated by factories, all over the country" New Research Trends in Material Science, The 5-th International Conference ARM-5, Sibiu, Romania, 5th –7th September, 2007

[7] *A. Diaconu, B.A. Sava, L.D. Ursu, I. Mitiu, E. Rosu, D. Radu, O. Dumitrescu, M. Eftimie* "Study on the recycling of borate silicate vitreous waste with capitalization of heavy metals sludge", Advanced Materials Research, **Vols. 39-40** (2008), pp 659-662, ISSN: 1022-6680

[8] *L.D. Ursu, Adriana Diaconu, B.A. Sava, L. Boroica, I. Mitiu, E. Rosu, D. Radu, M. Dinulescu, M. Eftimie,* "A study of the industrial waste incorporating in glass", Advanced Materials Research, **Vols. 39-40** (2008), pp 675-678**,** ISSN: 1022-6680

[9] *W.A. Weyl*, „ Coloured Glasses" Society of Glass Technology, Sheffield 1967

[10] *H.A. Silim*, "FTIR Spectroscopy and Structure of the Binary Glass Cu_2O – MoO_3 System", Egypt. J. Solids, **Vol. 28**, No. (1), (2005) 15

[11] *P.I. Paulose, G. Jose, V. Thomas, G. Jose, N.V. Unnikrishnan, M.K.R Warrier*, "Spectroscopic studies of Cu^{2+} ions in sol–gel derived silica matrix", Bulletin of Materials Science, **Vol. 25**, No. 1, pp. 69-74, February 2002.