

STUDII STRUCTURALE FTIR ȘI RAMAN ALE STICLELOR CU DEȘEURI DE CUPRU ȘI NICHEL FTIR AND RAMAN STRUCTURAL STUDIES OF GLASSES WITH COPPER AND NICKEL WASTES

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Present paper presents a study of the colorful glasses in the $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-K}_2\text{O-ZnO}$ system, to which there were added the borosilicate glass waste and copper oxide or nickel oxide from the sludge obtained from the electrochemical deposition industry. The use of borosilicate waste glass (that comes up with important components such as B_2O_3 , CaO , Al_2O_3), leads to saving of raw materials and energy while being sustainable at the same time. Structural studies of the obtained vitreous materials were made, using FTIR and Raman spectroscopy. FTIR absorption maxima and Raman shifts were identified and discussed according to literature data.

Lucrarea prezintă un studiu al sticlelor colorate din sistemul $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-K}_2\text{O-ZnO}$, în care s-au înglobat deșeurile de sticlă borosilatică respectiv oxid de cupru și de nichel proveniți din șlamurile rezultate în industrie la depunerile electrochimice. Folosirea deșeurilor de sticlă borosilatică (care aduc componenți importanți B_2O_3 , CaO , Al_2O_3), conduce la economii de materii prime și energie, fiind utilă și din punct de vedere al protecției mediului înconjurător. Au fost efectuate investigații structurale pentru materialele vitroase obținute prin metode spectroscopice FTIR și Raman. Maximele de absorbție FTIR și deplasările Raman au fost identificate și discutate comparativ cu datele din literatură.

Keywords: decorative glass, borosilicate cullet, copper containing sludge, nickel wastes, ftir, raman spectroscopy

1. Introduction

Oxide glasses are stable and this chemical stability, which is very good in time, led to the idea of using them as a suitable matrix for inerting the hazardous wastes, such as sludges with a high content of heavy metals. Vitrification of waste with other raw materials, is leading to a stable product which can be stored without environmental risks. This can turn through various processing techniques in products that can be use in various fields: fiber insulation or reinforcement, construction materials, aggregates for roads and other decorative products.

Recovery of glass cullets from the internal technological process or collected and reusing them in the batch mixture of raw materials for developing the vitreous matrix designed for recovery of pollutant waste is a direction that should be considered as having the important technical and economical advantages. Industrial development has led to diversification of by-products obtained in different industries, such as: machine-building industry, where results high quantity of waste with iron and chromium, that can be neutralized in the colorful bottles, in the proportions up to 30 (wt. %) [1-3]; leather processing industry, resulting high

amount of sludge containing various elements where the most dangerous being the chromium Cr(V), but that may be embedded in silico-calco-sodic glasses, resulting colored vitreous materials [4-9]; the pharmaceutical industry, with significant amounts of borosilicate glass waste, impregnated with different substances, but who can be valorified in colored glasses with applications in glazes and glass-ceramic [10-18].

Obtaining of glasses in the $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-K}_2\text{O-ZnO}$ system by recovery of borosilicate glass waste and wastewater treatment sludge (from electroplating process), respectively is a direction aligned to national policies of hazardous waste management which are in accordance with European ones. EU legislation establishes the importance of the recovery of by-products and neutralising toxic waste in accordance with Directive 2005/20/EC of 9 March 2005 on packaging and packaging waste (amending Directive 94/62/EC) and the Directive 2008/1/EC concerning integrated pollution prevention and control (amending Directive 96/61/EC), transposed into Romanian legislation.

Present paper presents a study of the structure of two series of glasses, which include waste with copper and nickel, respectively by FTIR

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and Raman spectrometry methods, in an attempt to elucidate the existence and the importance of glass structural changes due to the introduction of waste with a high content of copper and nickel.

2. Experimental part

The glasses from the $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-K}_2\text{O-ZnO}$ system were investigated. There were used three types of borosilicate waste (D1, D2 and D3) and copper oxide or nickel oxide recovered from sludge obtained from electrochemical deposition operations. Borosilicate glass cullets (having a thermal expansion coefficient in the range of $3.3\pm 5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), come from the pharmaceutical industry (white glass ampoules D1 and brown glass ampoules D3). Borosilicate glass waste D2, from laboratory equipments industry [19], components for the apparatus in the chemical industry and equipments for temperature and density measurement was used

There were obtained two series of glasses: RB5 and R4 (with three type of borosilicate waste D1, D2, D3 and copper oxide and nickel oxide, respectively). The RB5 and R4 glasses were obtained through the classical method of melting (into an electric oven–Nabertherm- equipped with superkanthal elements), at $1380 \text{ }^\circ\text{C}$ melting temperature. After that, the temperature was increased with $20 \text{ }^\circ\text{C}$, up to $1400 \text{ }^\circ\text{C}$ for the refining process, and it was maintained at this level for 2 hours. The melted glass cooling was conducted, from 1380°C to 1250°C , in 4 hours, average cooling rate being around $30^\circ\text{C}/\text{hour}$. The annealing treatment was done at $450 \text{ }^\circ\text{C}$, with a maximum speed of cooling rate of $15 \text{ }^\circ\text{C}/\text{h}$ mixed.

The oxide weight compositions (wt. %) for RB5 and R4 glass samples are presented in Table 1 and Table 2.

Characterization of these three types of borosilicate waste and sludge used (containing CuO and NiO), as well as the program of melting and annealing were presented in [20, 21]. Some properties such as: the linear coefficient of thermal expansion with the characteristic temperatures from thermal expansion diagrams, optical transmission in the visible and near infrared, hydrolytic stability, wetting capacity and viscosity were determined [20, 21].

For structural characterization of the RB5 and R4 glasses by FTIR and Raman spectroscopy, have been used glass powders from the two series of glasses, obtained by milling into an agate mill. The resulting powder has the grains size under $100 \text{ }\mu\text{m}$.

FTIR spectra were recorded with a Perkin Elmer Spectrophotometer-Spectrum 100, provided with UATR accessory (Universal Attenuated Total Reflectance) in the range $400\text{-}4000 \text{ cm}^{-1}$. The measurement error is $\pm 0.1\%$ and the number of scans 32.

Raman spectra were collected with a LabRAM HR 800 UV–VIS–NIR Horiba Jobin-Yvon spectrometer, at room temperature, acquired in the $100\text{-}2000 \text{ cm}^{-1}$ range. The samples were excited by Ar^+ laser excitation ($\lambda=514.5 \text{ nm}$) with a laser power at the sample surface of 2.6 mW , without an attenuation filter, focused on the surface sample with a confocal microscope, using an objective magnification $\times 100$, an exposure time of 2 s , an accumulation time of 5 s , five cycles, $1 \text{ }\mu\text{m}^2$ laser spot size, $0.5 \text{ to } 1 \text{ cm}^{-1}$ resolution and $1800 \text{ grating}/\text{mm}$ diffraction network.

Table 1

Oxide weight compositions of RB5 glasses (containing borosilicate waste and sludge with copper oxide)
Compozițiile oxidice (% grav.) ale seriei de sticle RB 5 (cu deșeu de sticlă borosilicatică respectiv oxid de cupru provenit din nămol)

Composition (wt %) Compoziție (grav.%)	SiO ₂	CaO	BaO	Na ₂ O	K ₂ O	Al ₂ O ₃	B ₂ O ₃	ZnO	Fe ₂ O ₃	CuO	TiO ₂	Σ
RB 5.1.0.0	61.48	-	-	19.45	3.13	0.82	2.00	12.81	-	0.31	-	100
RB 5.1.1.15	61.15	0.10	0.02	19.57	3.18	0.93	1.99	12.75	-	0.31	-	100
RB 5.1.1.30	60.73	0.20	0.04	19.64	3.22	1.23	1.97	12.66	0.01	0.31	-	100
RB 5.1.1.43	64.78	0.26	0.05	17.53	2.89	1.24	1.76	11.20	0.01	0.27	-	100
RB 5.1.2.15	61.30	0.02	0.01	19.54	3.14	0.92	1.99	12.78	-	0.31	-	100
RB 5.1.2.30	61.11	0.04	0.02	19.62	3.15	1.01	2.00	12.74	-	0.31	-	100
RB 5.1.3.15	60.99	0.07	0.08	19.46	3.17	1.03	1.99	12.71	0.04	0.31	0.14	100
RB 5.1.3.30	60.53	0.15	0.15	19.48	3.21	1.22	1.97	12.62	0.08	0.30	0.28	100
RB 5.1.3.45	64.51	0.19	0.20	17.33	2.89	1.26	1.74	11.13	0.11	0.27	0.37	100

Table 2

Oxide weight compositions of R4 glasses (containing borosilicate waste and sludge with nickel oxide)
 Compozițiile oxidice (% grav.) ale seriei de sticle R4 (cu deșeu de sticlă borosilicatică respectiv oxid de nichel provenit din nămol)

Composition (wt.%) Compoziție (grav.%)	SiO ₂	CaO	BaO	Na ₂ O	K ₂ O	Al ₂ O ₃	B ₂ O ₃	ZnO	Fe ₂ O ₃	TiO ₂	NiO	Σ
R 4.1.0.0.	61.62	0.00	0.00	19.49	3.13	0.83	2.01	12.84	0.00	0.00	0.083	100.00
R 4.1.1.15	61.23	0.10	0.02	19.59	3.18	1.03	1.99	12.77	0.00	-	0.08	100.00
R 4.1.1.30	60.87	0.20	0.04	19.68	3.22	1.23	1.98	12.69	0.01	-	0.082	100.00
R 4.1.2.15	63.42	0.02	0.01	20.22	0.02	0.95	2.06	13.22	-	-	0.09	100.00
R 4.1.2.30	61.25	0.04	0.02	19.67	3.15	1.01	2.00	12.77	-	-	0.08	100.00
R 4.1.3.15	61.13	0.07	0.08	19.51	3.18	1.03	2.00	12.74	0.04	0.08	0.14	100.00
R 4.1.3.30	60.67	0.15	0.15	19.53	3.22	1.23	1.97	12.65	0.08	0.08	0.28	100.00

3. Results and discussions

Recorded FTIR spectra for the series of RB5 and R4 glasses (with borosilicate waste cullets D1, D2, D3 and copper oxide or nickel oxide from sludge) are presented in the figures 1÷6.

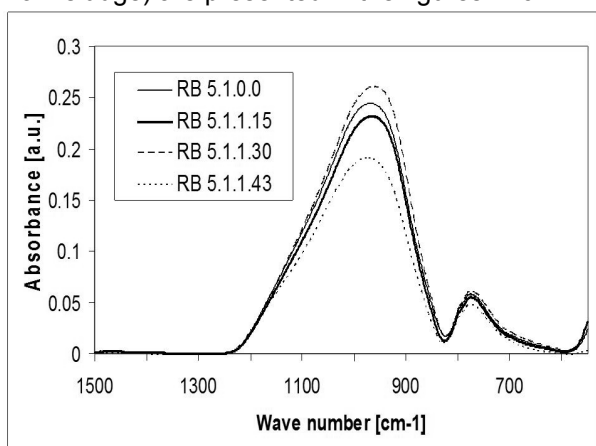


Fig.1 - IR absorption spectra for RB5 glasses with borosilicate waste D1 / Spectrul de absorbție IR al seriei de sticle RB 5 cu deșeu D1 și oxid de cupru.

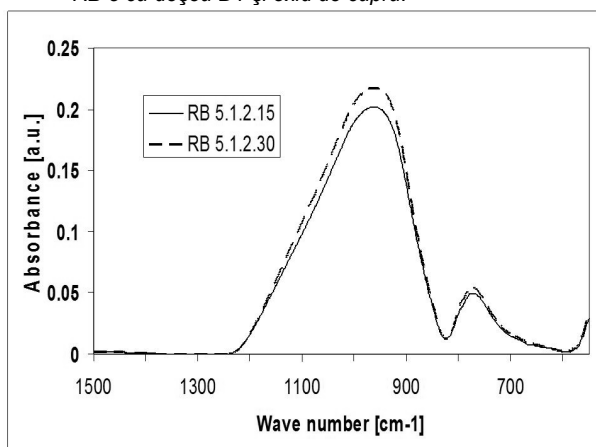


Fig.2 - IR absorption spectra for RB5 glasses with borosilicate waste D2 / Spectrul de absorbție IR al seriei de sticle RB 5 cu deșeu D2 și oxid de cupru.

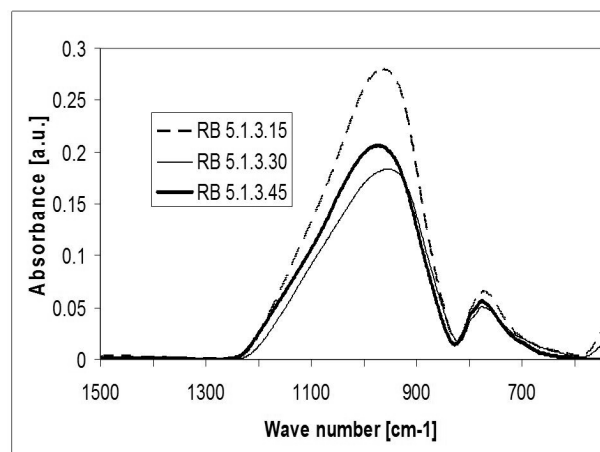


Fig.3 - IR absorption spectra for RB5 glasses with borosilicate waste D3 / Spectrul de absorbție IR al seriei de sticle RB 5 cu deșeu D3 și oxid de cupru.

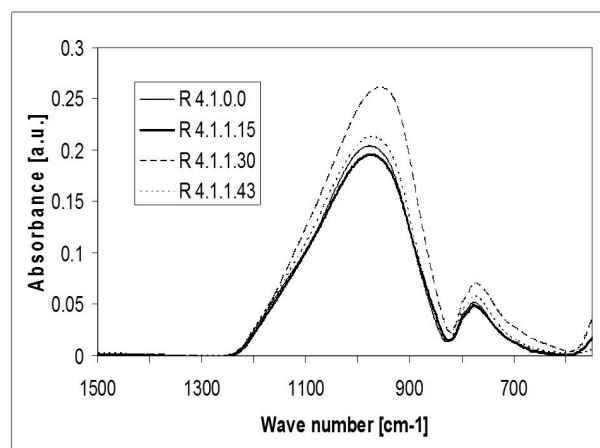


Fig.4 - IR absorption spectra for R4 glasses with borosilicate waste D1 / Spectrul de absorbție IR al seriei de sticle R4 cu deșeu D1 și oxid de nichel.

In the case of the investigated glasses (table 3) the variation of Si and B concentration in their composition is small.

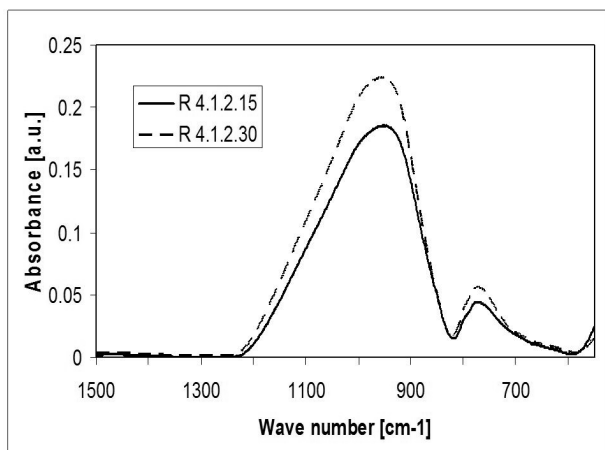


Fig.5 - IR absorption spectra for R4 glasses with borosilicate waste D2 / Spectrul de absorbție IR al seriei de sticle R4 cu deșeu D2 și oxid de nichel.

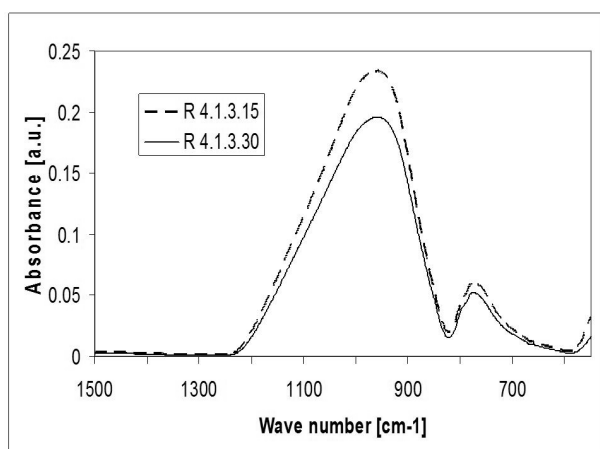


Fig.6 - IR absorption spectra for R4 glasses with borosilicate waste D3 / Spectrul de absorbție IR al seriei de sticle R4 cu deșeu D3 și oxid de nichel.

FTIR spectra do not show major differences. All the spectra present two characteristic peaks at the band around 773 cm^{-1} and 965 cm^{-1} . The bands around 773 cm^{-1} , are assigned to B-O-B linkage

bending vibrations in the glass structure and to isolated BO_3^{3-} triangle groups. The bands around 965 cm^{-1} , are assigned to B-O bonds stretching vibrations in $[\text{BO}_4]$ units from diborate groups [22, 23, 27], [22, 23, 24] to stretching vibration of B-O-Si linkage and to asymmetric stretching vibrations of the Si-O-Si bonds [22, 23]. Variations of 5 cm^{-1} (for absorption band centered around 773 cm^{-1}) and 28 cm^{-1} (for absorption band centered around 965 cm^{-1}) were due to small variations of Si and B in the compositions of glasses, with the formation of BO_3^{3-} , $[\text{BO}_4]^-$ and B-O-Si and Si-O-Si structures, respectively in local concentrations slightly different and with changing of polymerization degree of vitreous structure.

A deconvolution of the large absorption band from around 960 cm^{-1} (Figure 7) shows the existence of three absorption bands the absorption band which appeared at 1121 cm^{-1} and the shoulder at 925 cm^{-1} are attributed to the stretching modes of $(\text{BO}_4)^{-1}$ tetrahedral boron and the stretching vibrations of the Si-O-Si bonds at 1005 cm^{-1} , respectively [30]. [25]

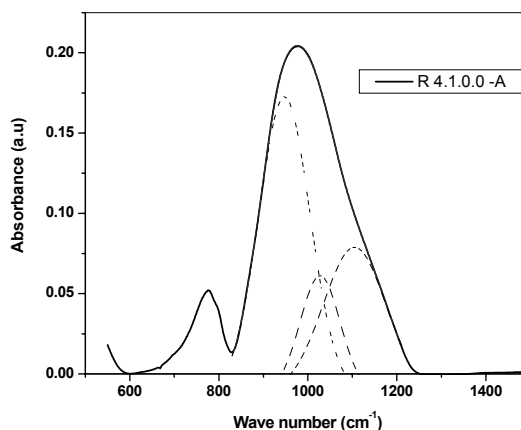


Fig. 7 - The deconvolution of the peak centered around 960 cm^{-1} / Descompunerea maximului de absorbție centrat în jurul valorii de 960 cm^{-1} .

Table 3

Assignment of IR absorbance spectra of RB5 and R4 glasses
Atribuirea spectrelor de absorbție IR pentru sticlele RB5 și R4

Sample Proba	cm^{-1}	Attribution Atribuire	cm^{-1}	Attribution Atribuire
4.1.0.0	776	B-O-B linkages bending in borate network and isolated BO_3^{3-} triangle groups [22,23]	979	-B-O bonds stretching vibrations in $[\text{BO}_4]$ units from diborate groups [22] -stretching vibration of B-O-Si linkage [23] - asymmetric stretching vibrations of the Si-O-Si bonds [23]
4.1.1.15	776		975	
4.1.1.30	775		959	
4.1.1.43	776		972	
4.1.2.15	771		951	
4.1.2.30	771		955	
4.1.3.15	775		959	
4.1.3.30	775		959	
RB 5.1.0.0	776		967	
RB 5.1.1.15	775		967	
RB 5.1.1.30	775		963	
RB 5.1.1.43	775		975	
RB 5.1.2.15	775		963	
RB 5.1.2.30	775		963	
RB 5.1.3.15	775		963	
RB 5.1.3.30	776		955	
RB 5.1.3.45	776		975	

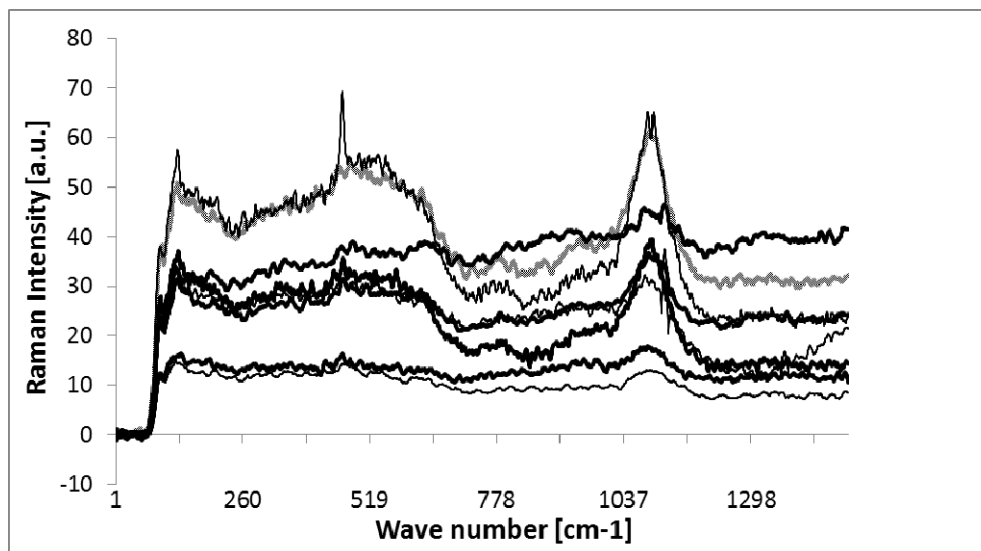


Fig. 8 - Raman spectra for RB5 glasses / Spectrele Raman pentru sticlele din seria RB5.

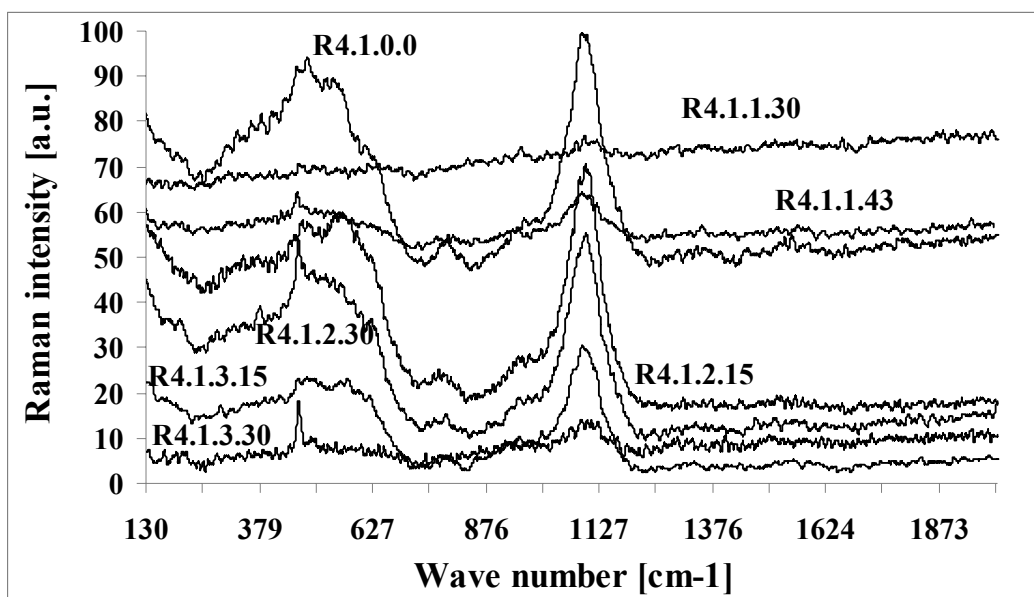


Fig. 9 - Raman spectra for R4 glasses / Spectrele Raman pentru sticlele din seria R4.

The variations of the absorption peak centered around 960 cm^{-1} and showed in all samples due to the variations of those 3 maximum absorption attributed of stretching modes of $(\text{BO}_4)^{-1}$ tetrahedral and stretching vibrations of the Si-O-Si bonds are due to local compositional variations.

Raman spectra recorded in the range from $100\text{--}2000\text{ cm}^{-1}$ for the series of RB5 and R4 glasses are given in figure 8 and figure 9. Analysis of these spectra show a maximum for boron oxide polymerized $[\text{BO}_4]$ located around 1080 cm^{-1} . Boroxol type rings specific for pure boron oxide (which appear in the structure of many glasses) and the borate triangles $[\text{BO}_3]^{-3}$, are put in evidence at 700 cm^{-1} maximum. The peaks due to poliborates (tri-, tetra-pentaborates) appear between 700 and 1300 cm^{-1} . The Raman maximum at 1300 cm^{-1} is characteristic for pyroborates. The specific peaks for Si-O vitreous

appear in all cases at the wave numbers between 400 and 900 cm^{-1} . Symmetric stretching vibrations ν_1 for Si-O are put in evidence in all the cases in the range of $810\text{--}848\text{ cm}^{-1}$, and asymmetric stretching vibrations Si-O ν_3 appear for Q2 type species around 1080 cm^{-1} . For Q3 species the maximum for symmetric stretching appears to $1100\text{--}1106\text{ cm}^{-1}$. In all investigated cases are the peaks due to Q2 and Q3 groupings, with minor variations for compositional investigated changes.

4. Conclusions

There were obtained several glasses in order to reuse the waste with a high content of copper and nickel oxides, through their introduction in the glassy borosilicate matrix, obtained by reusing of borosilicate waste.

The structure of obtained glasses was investigated by FTIR and Raman spectroscopy.

The introduction of the waste did not bring significant influences on the structure of vitreous matrix. There were emphasized evidence several types of borate structures, including BO_3^{3-} groups and many types of borates, confirmed by the two methods of structural analysis.

Out of silicatic groups there were put in evidence mainly Q2 and Q3 type.

FTIR absorption maxima and Raman shifts showed insignificant changes with changing composition of borosilicate waste and with the introduction of a high content of copper and nickel oxide. The conclusion shows that the waste has been incorporated into the basic vitreous matrix, without significant structural changes of the matrix.

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