STUDIU PRIVIND STICLELE BOROSILICATICE CU TRANSMISIE ÎN UV
STUDY ON BOROSILICATE GLASSES WITH UV TRANSMISSION

MIHAI-ALEXANDRU EFTIMIE[1], CARMEN-CRISTINA UDREA[1], MIHAELA-ALINA MELINESCU[1]*, ANA-VIOLETA FILIP[2]

[1] National University of Science and Technology Politehnica of Bucharest, Faculty of Chemical Engineering and Biotechnologies, Department of Science and Engineering of Oxide Materials and Nanomaterials, 1-7 Polizu str., Bucharest, Romania

[2] National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor str., Magurele, Ilfov, Romania

Borosilicate glasses that possess UV transmission can be used in materials that facilitate the disinfection or inactivation of bacteria using UV light. Three compositions were elaborated in the low alkali domain of borosilicate glasses through the classical melt-quenching technique at temperatures up to 1680 °C. The analysis of the samples was performed using thermal expansion, hydrolytic stability, density, UV-Vis transmission, Raman spectroscopy, and X-ray diffraction. The hydrolytic stability of the analysed samples showed that they are chemically stable. From the thermal expansion it was observed that the processed samples had low expansion coefficients. Regarding the UV-Vis transmittance, glasses have acceptable transmittances in the ultraviolet region down to 260 nm. Raman spectroscopy was used to identify the glass network bonds and the presence of nonbridging oxygen ions in the processed glass samples by the presence of specific high-frequency peaks in the spectrum. XRD analysis also showed that the borosilicate glass samples did not crystallize.

Sticlele borosilicatice cu transmisie în UV pot fi utilizate în materiale care facilitează dezinfectarea sau inactivarea bacteriilor cu ajutorul luminii UV. Au fost elaborate trei compoziții de sticle borosilicatice cu conținut scăzut de alcalii prin tehnica clasică de topire-subrăcire la temperaturi de până la 1680 °C. Analiza probelor a fost realizată cu ajutorul dilatării termice, a stabilității hidrolitice, a densității, a transmisiei UV-Vis, a spectroscopiei Raman și a difracției de raze X. Stabilitatea hidrolitică a probelor analizate a indicat că acestea sunt stabile din punct de vedere chimic. Din dilatarea termică s-a observat că probele obținute au avut coeficienți de dilatare mici. În ceea ce privește transmitanța UV-Vis, sticlele au transmitanțe acceptabile în regiunea ultravioletă până la 260 nm. Spectroscopia Raman a fost utilizată pentru a identifica legăturile din rețeaua vitroasă și prezența ionilor de oxigen nepuntați în probele de sticlă prin prezența unor vârfuri specifice de înaltă frecvență în spectru. Analiza XRD a indicat, de asemenea, că probele de sticlă borosilicatică nu au cristalizat.

Keywords: *borosilicate glass, UV-Vis transmission, germicidal applications*

1.Introduction

Borosilicate glasses are known for their low thermal expansion, high chemical durability, and high electrical resistivity [1]. These properties make them suitable for various scientific and industrial applications, such as laboratory glassware, cookware, lighting, electronics, and sealing [1]. One of the emerging applications of borosilicate glasses is in germicidal devices, which use ultraviolet (UV) radiation to kill or inactivate microorganisms such as bacteria, viruses, and fungi. UV light between 100 and 280 nm (UVC) is the most effective band for germicidal purposes, as it can damage the DNA and RNA of microorganisms and prevent them from reproducing [2]. Borosilicate glasses are good candidates for germicidal applications because they have high transmittance of UV radiation [1]. Borosilicate glasses also have high resistance to UV-induced degradation, which means they can maintain their mechanical and optical properties even after prolonged exposure to UVC radiation [1, 2]. This ensures that the glass material does not crack, or lose its transparency over time. Moreover, borosilicate glasses have high thermal shock resistance, which means they can withstand rapid changes in temperature without breaking or cracking. This is important for germicidal devices that may operate at high temperatures or experience frequent on-off cycles.

Shou et al. [3] revealed the relationship between the content of Al_2O_3 and B_2O_3 and the impacts on the units of glass network, and the relationship between the effects of the units of glass network and the chemical stability and the UV transmittance of the borosilicate glasses with concentrations of B_2O_3 up to 13 wt. %. Higher concentrations of B_2O_3 induced excellent chemical stability, while the UV transmittance of glass samples gradually decreased with increasing Al_2O_3 content, and the UV transmittance of glass samples increased first and then decreased with increasing B_2O_3 content.

A recent report from Wangling et al. [4] indicated that iron oxidation state in or out of the produced glass has a significant effect on the boron-

* Autor corespondent/*Corresponding author*,
E-mail: alina.melinescu@gmail.com

oxygen structure of alkali-borosilicate glass and on the UV transmittance at a wavelength of 254 nm, the UV absorption coefficient of ferric ion (Fe(III) being about four times greater than that of ferrous ion Fe(II)) at 254 nm.

Technical glasses for the UV region were also studied in an ample report of D. Ehret [5], who stated that, to achieve a higher UV transmission, it is necessary to minimize the Fe^{3+} content in the glass. One way is the use of expensive raw materials with low iron content, another, the reduction of Fe^{3+} to Fe^{2+} through reducing melting conditions, which allowed Ehret to report high UV transmission in the UVB region (280 to 315 nm).

Literature reports some patents dealing with borosilicate glasses, claiming high UV transmission, like US5547904A patent [6], with borosilicate glasses with UV transmission of at least 80% at a UV wavelength of about 254 nm for a borosilicate glass sheet thickness of 2 mm.

Here we report the results of an investigation on UV-Vis transmission of some borosilicate glasses with low alkali content and melting temperatures as low as 1600 °C, elaborated through the classical melt-quenching technique. Sample analysis was carried out using X-ray diffraction to confirm their vitreous characteristics, and UV-Vis transmission to assess the light transmission down to 250 nm, which allows the studied glasses to be used in germicidal applications.

2. Materials and methods

In this study, borosilicate glasses were synthesized through classic melt quenching route. The nominal gravimetric compositions of the synthesized glasses are presented in Table 1. The raw materials were analytical grade silica (SiO_2), boric acid (H_3BO_3), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), lithium carbonate (Li_2CO_3), zinc oxide (ZnO) and alumina (Al_2O_3). The compositions were chosen to have high concentrations of B_2O_3 to lower the melting temperature, while Na_2O, K_2O and Li_2O lowered the viscosity of melts for a good fining process. Al_2O_3 and ZnO were added to increase the stability of glasses.

The raw materials were weighed on an analytical balance and dry-homogenized in a mortar for 10 minutes. As the melting temperatures were not known, they were estimated, so the borosilicate glasses were melted at different temperatures between 1600 and 1700°C due to compositional differences and depending on the viscosity of the melts.

The melting process was carried out in alumina crucibles into a NABERTHERM 3000 electric furnace and in the absence of any type of melting accelerator or refiner, the no. 3 glass melt had gas bubbles trapped even after a 3-hour plateau. Casting of the 20x20 x5 mm samples took place in a graphite form.

The annealing temperatures were estimated based on melting temperatures, then established through dilatometry and the samples were annealed again in a CARBOLITE 100 oven with 1 hour plateau at the annealing temperature specific for each glass sample, with 1°C/min decrease rate down to strain temperature, then the samples were left to cool in the annealing oven.

Density was measured using a RADWAG balance and Archimede's method. Thermal expansion and specific temperatures were obtained using a DIL402 PC dilatometer from NETZSCH, Germany with 3°/min rate, in air. Chemical stability was assessed measuring the conductivity of a solution made of water and grinded glass, at constant temperature, for 2 hours, using an AGILENT 3200C conductivity meter. The glass samples were grounded in a porcelain mortar, then passed through two sieves with different mesh sizes. The fraction between the two sieves was chosen. The closer the sieves mesh sizes are to each other, the less polydisperse the grain size fraction between the two sieves will be and the more constant the average fraction size (i.e. its specific surface area) will be from one glass sample to another. From this fraction 1 g was weighed on the analytical balance and then mixed with 50 ml of distilled water in a Berzelius beaker.

The mix was continuously stirred for 120 minutes at 25 °C and its electrical conductance was measured with the aid of the conductivity meter every minute for the first 5 minutes, then every 5 minutes for the remaining time. The conductance of distilled water was previously measured at the same temperature and was subtracted from all the glass-water mix measurement values.

UV-Vis spectroscopy was carried out using a UV-160A Shimadzu spectrometer. Borosilicate glass samples were prepared and polished

Table 1

Glass compositions / *Compozițiile sticlelor*

Glass sample	Glass code	Oxide (wt. %)						
		SiO_2	B_2O_3	Na_2O	K_2O	Al_2O_3	Li_2O	ZnO
1	UV1	65.0	25.0	3.0	2.0	5.0	0	0
2	UV2	62.7	26.9	6.6	0	3.5	0	0
3	UV3	72.0	25.0	0.5	1.0	1.0	0.5	0
4	UV4	69.0	18.5	1.0	7.5	3.0	0.5	0.5

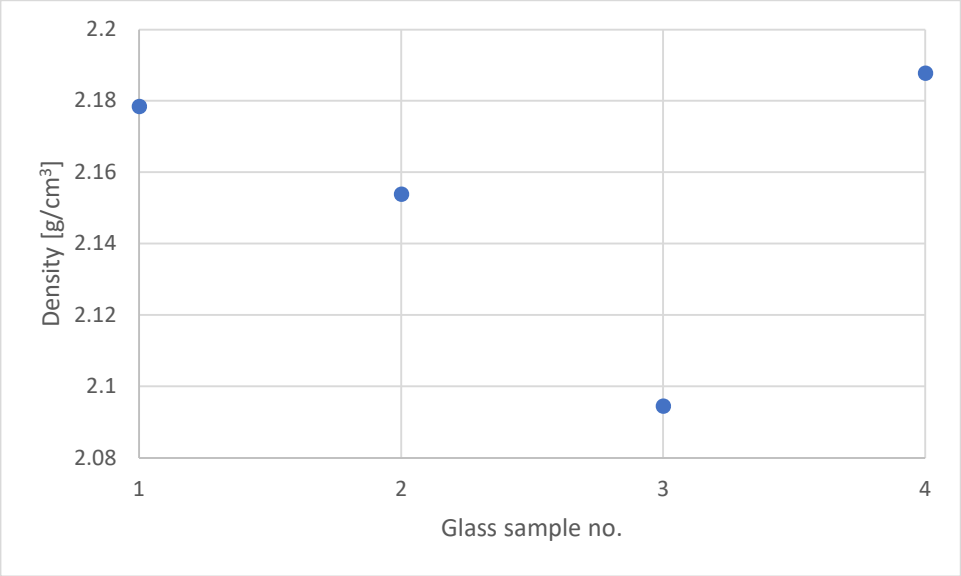

Fig. 1 - Glass sample densities / *Densitățile probelor de sticlă*

for UV-Vis analysis on a high-performance machine. The thickness of the samples was 4 mm.

For XRD measurements to confirm the vitreous state of the samples, a BRUKER D8 ADVANCE USA type X-ray diffractometer (Cuka$_\alpha$, λ= 1.54 Å) was used. The X-ray pattern was acquired at room temperature, using a step of 0.02° and 5 s integration time, the scan being done between 10° and 70° (2θ range). ICDD powder Diffraction database was used for phase identification, while Raman spectra in the 100–1800 cm^{-1} range were gathered with the aid of a Labra HR Evolution HORIBA, France, acquisition time 2s, accumulation 20, 514 nm laser, the measurement error of ±0.5 cm^{-1}.

3.Results and discussion

3.1. Density

The density of a glass is the mass per unit volume (if the homogeneity condition is met).

$$d = \frac{m}{V} \quad g/cm^3 \quad (1)$$

where: d – density, m – mass, V - volume.

The density was determined experimentally by hydrostatic weighing. The method consists of measuring the mass of the sample in air and immersed in a liquid (distilled water) of known density at working temperature. Hence, formula 1 becomes:

$$d = \frac{m_{air}}{m_{air} - m_{liquid}} \cdot d_{liquid} \quad (2)$$

where: d – density, m_{air} – mass of the sample weighted in air, m_{liquid} – mass of the sample weighted in water, d_{liquid} – density of the water at room temperature.

Knowing the density of water at the working temperature of 20°C, 0.99823 g/cm^3, the densities of borosilicate glass samples are obtained.

The densities obtained for borosilicate glass samples have closer values, as depicted in Figure 1. However, glass sample no. 3 has a lower density value compared to the other samples. This can be explained by the chemical composition that glass no. 3 has. Unlike the other three samples, where the mass percentage of Al_2O_3 varies between 3-5%, sample 3 contains a much lower mass percentage of Al_2O_3, of 1%. Since the molecular mass of alumina is 102 g/mol, a lower percentage of Al_2O_3 determines the density of the glass to decrease.

On the other hand, glass sample no. 3 had a much higher number of gas bubbles compared to the other four samples, which, for the same volume, decreases the mass and, therefore, the density of the sample, which becomes apparent density for this sample, due to the trapped bubbles.

3.2. Thermal properties

The thermal expansion curve measured by dilatometry in Figure 2 gives important properties: the coefficient of thermal expansion (α), the glass structural transformation temperature or glass transition temperature (Tg), annealing and strain temperature (T_{SR} and T_{IR}), and the dilatometric softening temperature (T_D), as presented in Table 2.

It can be seen from the thermal expansion curves that the experimentally developed samples had very low coefficients of thermal expansion for a borosilicate glass, around $2 \cdot 10^{-6}$-$4 \cdot 10^{-6}$ K^{-1}, which make the glasses capable to resist to thermal shocks that are sometimes induced in the germicidal systems, as well as low and close glass transition and dilatometric softening temperatures, which correlate with the low content of alkali oxides.

3.3. Chemical stability

Chemical reactions with glass surfaces, induced by exchange, erosion, or adsorption

Table 2. Thermal properties of the glass samples / *Proprietățile termice ale probelor de sticlă*

Glass sample	Thermal expansion, α_{20}^{300}*10^6, [K^{-1}]	Strain temperature, T_{IR}, °C	Glass transition temperature, Tg, °C	Strain temperature, T_{IR}, °C	Dilatometric softening temperature, T_D, °C
1	3.63	490	513	537	554
2	4.39	443	477	502	544
3	2.80	453	483	507	548
4	3.91	421	492	520	549

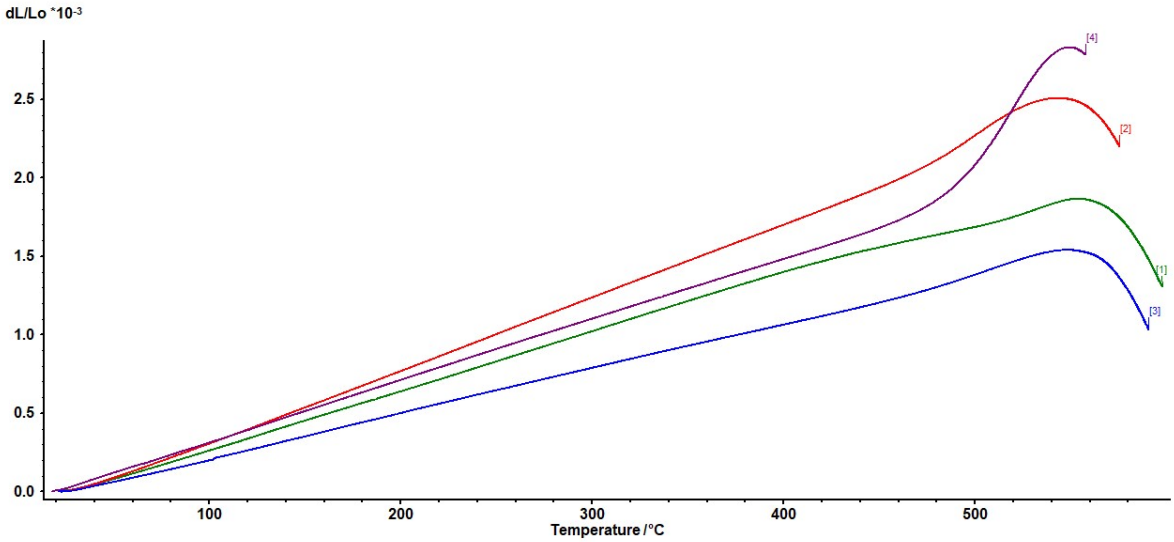

Fig. 2 - Thermal expansion curves of the glass samples / *Curbele de dilatare termică a probelor de sticlă*

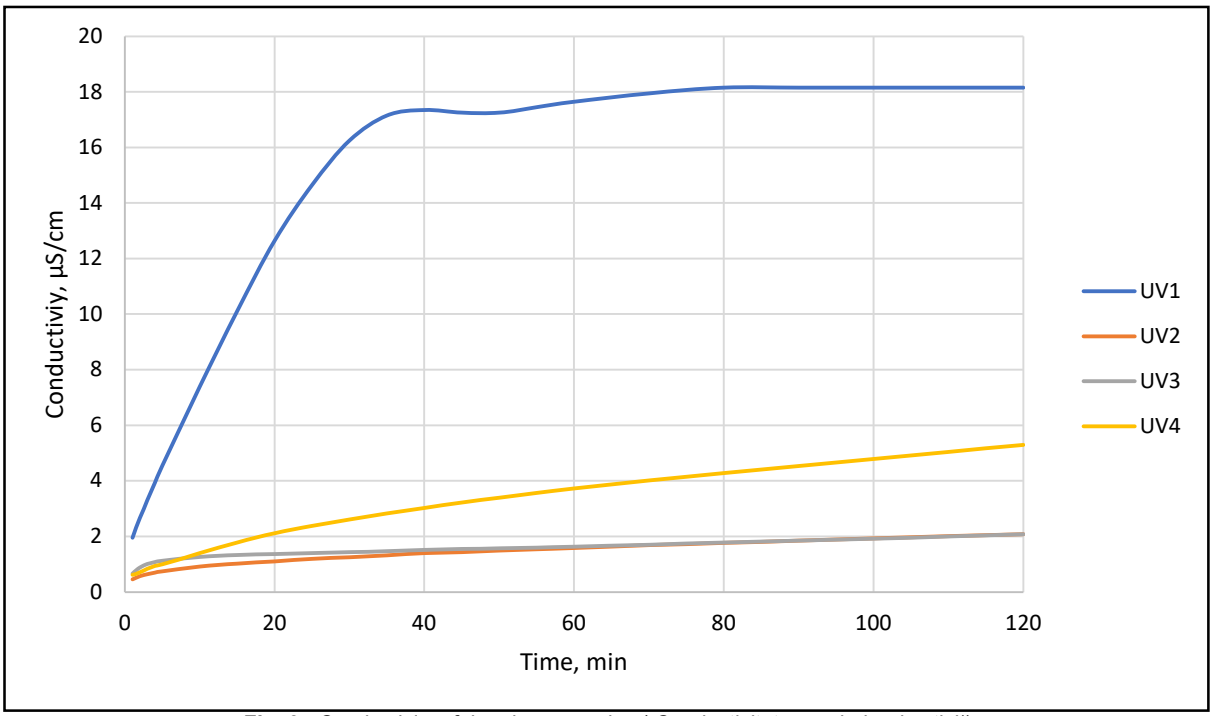

Fig. 3 - Conductivity of the glass samples / *Conductivitatea probelor de sticlă*

processes, can cause a wide range of effects, from virtually invisible surface changes to opacity, staining, thin films with interference colours, crystallization etc. These changes are often limited to the surface of the glass, but in extreme cases can destroy or completely dissolve the glass. The composition of the glass, the contact environment and the operating conditions will decide to what extent these chemical attacks are technically significant [7].

For germicidal applications, glass must be resistant to different chemical solutions so that multiple reactions can take place without the risk of damaging the glass or equipment. In addition, no disturbing amounts of glass components should be released into the reaction chamber. Acid attack is of particular importance both in laboratories and in chemical technology.

The assessment of the kinetics of the water attack process on glass is very necessary. Such an evaluation can be made using the conductivity method. This measures the variation of the electrical conductance of a suspension of glass powder in water as a function of time, keeping constant from one determination to the other the temperature, the amount of glass powder and its specific surface area, and the amount of water in the suspension (hence the concentration of the suspension). The method has the advantage of measuring the kinetics of the process of attack of the glass by the water, revealing whether this process stops over time (stabilization process) or evolves continuously without stopping (corrosion process).

The results are presented in Figure 3. The hydrolytic stability of the analysed samples shows that they are chemically stable, with conductivities below 30 μS/cm. Sample 1 has the highest conductivity value, which means that it had a rapid release of ions in the first hour and then it stabilizes. Samples 2, 3 and 4 show lower conductivity values, have a slow but quasi-constant release of ions, even after two hours of analysis.

A lower conductivity means a very good chemical stability, which makes the glasses chemically resistant to different substances and solutions, as well as to different germicidal applications.

3.4. UV-Vis spectroscopy

The UV-Visible absorption behaviour of glasses is useful for studying optical properties, electronic transitions, electronic polarizability, and bonding character in glass lattices due to the optical band gap of different glass compositions. In addition, electronic transitions induced by the optical band structure of glass materials are investigated. The different types of electronic transitions between the valence band and the conduction band are direct and indirect transitions [8].

The results presented in Figure 4 indicate that glass sample no. 3 shows no transmission in the UV region, having a maximum transmission of ~ 85% at 360 nm wavelength in the visible range.

Samples 1, 2 and 4 showed a transmission around 25-28% at 290 nm wavelength in the UV range. Sample 1 had a maximum transmission of ~ 75% at ~ 400 nm wavelength in the visible range.

The obtained values in the UV region are quite good, considering the thickness (literature data uses 2- or 3-mm thick samples) and can be associated with the structure of the glass through the presence of bubbles and streaks, and with the composition (alkali oxides and alumina), which decreases the UV transmission.

3.5. *Raman spectroscopy*

Raman spectroscopy is ideal for identifying the glass lattice, especially in the high-frequency regime (850-1200 cm^{-1}) [9], which corresponds to the Si-O elongation modes of Q^n species.

The bands at 1065.3, 1066.4 and 1061.8 cm^{-1} and 1163.2, 1166.7 and 1159.7 cm^{-1}, respectively, from figure 5, are attributed to Si-O elongation in a tetrahedron with an unpaired oxygen next to a fully bound tetrahedron in the silicon lattice [9]. It is important to note, however, that conventional structural models of borosilicate glasses with alkali oxides suggest that there should be no non-bridging oxygens (NBO) in this compositional range [10]. The total NBO concentration is probably less than 1 or 2% of the total oxygen and therefore the concentrations of the corresponding Si and B species should also be quite low, although possibly detectable by Raman spectroscopy.

The Raman bands at 461.4, 463.7 and 459 cm^{-1} were attributed to the vibrational mode of Si-O-Si bond bending in six tetrahedron cycles [9].

The bands at 800 cm^{-1} are attributed to the symmetric elongation of the O-Si-O bonds, associated with Si (possibly and B) displacements relative to its surrounding oxygens [10].

The bands at 927.7, 927.9 and 928.9 cm^{-1} are attributed to Si-O elongation vibration with two NBO atoms on a silicon atom [9].

3.6. XRD spectra

The XRD spectra is depicted in Figure 6. Borosilicate glass samples present a wide shoulder corresponding to the glassy phase in the system for every sample.

The XRD pattern shows only one diffraction peak with a large width for each sample, with no peaks associated with any crystalline phase, verifying the amorphous nature of the glass samples. It is observed that the width of the diffraction peaks increases as the silica content increases.

Also, the background noise is increased for each sample, which proves the amorphous state of the processed borosilicate glasses.

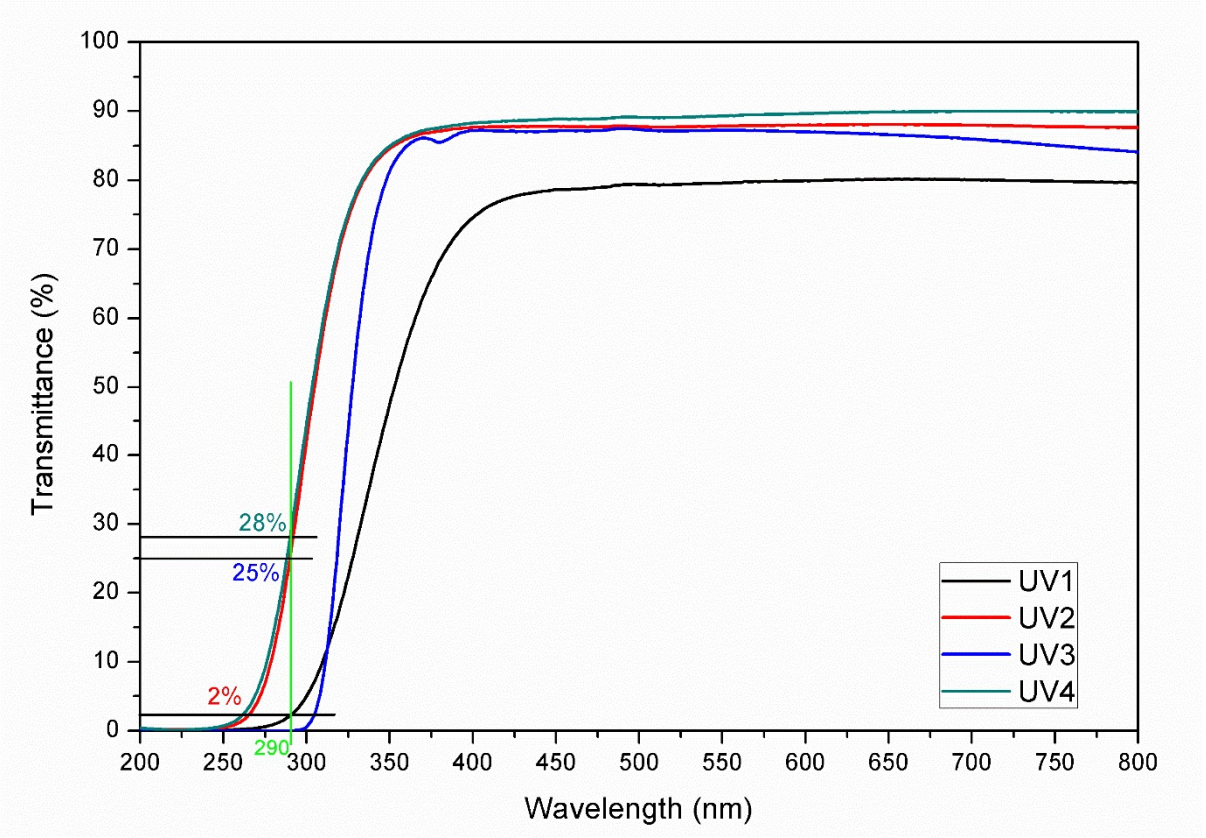

Fig. 4 - UV-Vis transmittance of the glass samples / *Transmisia UV-Vis a probelor de sticlă*

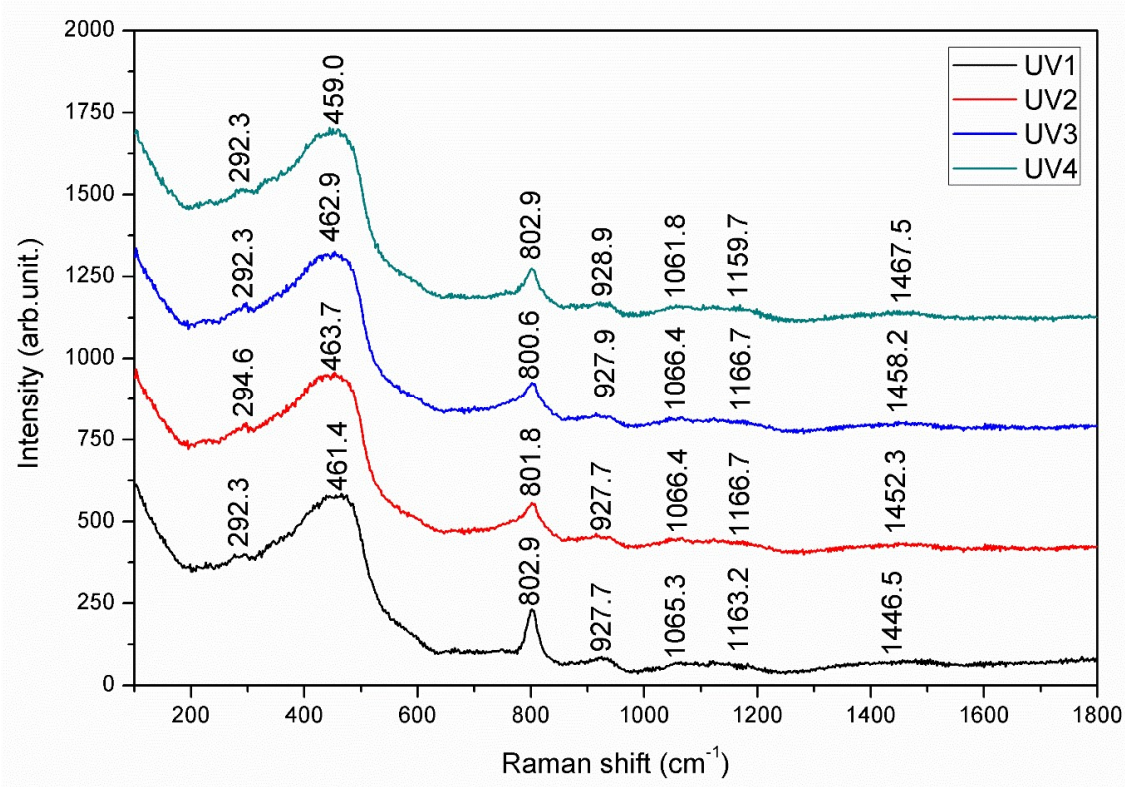

Fig. 5 - Raman spectra of glass samples / *Spectrele Raman ale probelor de sticlă*

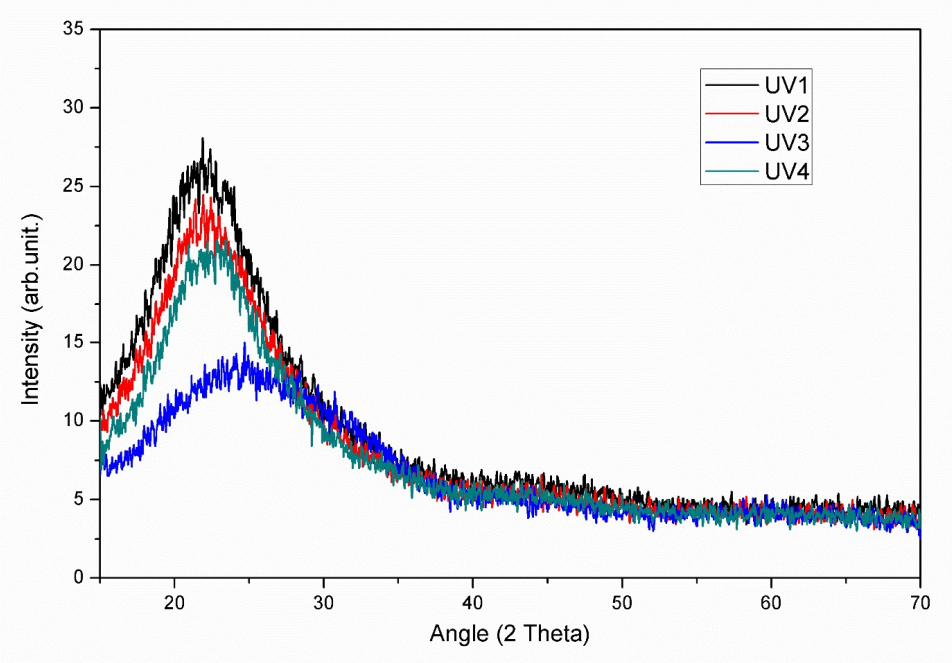

Fig. 6 - XRD spectra for glass samples / *Spectrele XRD ale probelor de sticlă*

4.Conclusions

Improved borosilicate glasses have been obtained with good transmission of electromagnetic radiation in the UV-Vis region, low thermal expansion coefficient and high chemical stability, making them important for various applications such as germicidal UV lamps, photomultipliers, spectrophotometers etc.

The density of the samples showed similar values for the 5 samples developed. The hydrolytic stability of the analysed samples showed that they are very stable. From the thermal expansion the processed samples had low expansion coefficients, between $20 \cdot 10^{-7}$ - $40 \cdot 10^{-7}$ K^{-1}. For the UV-Vis transmission, the analysed samples had excellent transmissions in the visible range, with a maximum transmission of 75-85% at wavelengths of 290-400 nm, making them suitable materials for applications of visible light and in the ultraviolet region, considering the 4 mm thickness of the samples, the morphology of the glasses which contain some bubbles and streaks, and the alkali oxides that lower the transmission of UV light. Raman spectroscopy was used to identify the glass lattice, the presence of non-bridging oxygen ions in the processed glass samples by the presence of specific peaks in the spectrum. XRD analysis also showed that the borosilicate glass samples did not crystallize, while the presence of a wide shoulder for each sample verifies the amorphous nature of the processed glass.

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