

SILVER DIFFUSION AND COLORATION OF SODA LIME AND BOROSILICATE GLASSES PART 1: EFFECT ON THE TRANSMISSION AND COLORATION OF STAINED GLASSES

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Using the conventional method of coloration, soda lime and borosilicate glasses have been painted. Once stained, these glasses were heat treated at temperatures close to their transition temperatures (T_g). A parametric study was carried out in order to determine at first the effect of the silver concentration in the stain spread on glass. In addition, it was studied the effect of the heat treatment duration and the chemical composition of the painted glasses on the formation and size of the silver nanoparticles, the silver diffusion depth and also the glasses coloration. The characterization was made using UV-Vis spectroscopy, Raman confocal spectroscopy, SEM, EDX Technique and Abbe Refractometer. The obtained results shows that the coloration intensity of both glass types painted by the conventional method differs and depends essentially on the proportion of alkali ions in the glass. Moreover, it was found that the effect of the silver concentration in the stain is primordial and the heat treatment duration has a limited effect.

INTRODUCTION

Glasses containing silver ions have long been used because of their importance in science and technology, these glasses have attracted much interest for decades. The great interest on these materials is motivated by their high ionic conductivity enabling their potential use as solid electrolytes employed as fuel cell [1] and in electrochemical devices [2-4]. Glasses doped with silver are also of interest because they have several advantages over their crystalline counterparts; among other they offer an isotropic conductivity [5]. Thin-film battery using the ionic conductivity of glasses can be manufactured and allow new applications in microelectronics [6]. Moreover, these glasses can be employed in optoelectronic devices such as waveguides [7, 8] and microlenses [9].

The glasses containing silver ions have also been used as antibacterial and antimicrobial inorganic materials [10-15] that may destroy the bacteria. Indeed, it was shown that silver glass can kill the AIV virus, and after the pneumonia that threatened the world in the first half of 2003, it was shown that these glasses also destroy the coronary virus 'SARS' [15].

On the other hand, it is well known that silver nanoparticles have been used for centuries as a yellow tint for glasses, which made the silver a revolutionary colorant used to paint the windows of the religious places [16-17].

An ion exchange non conventional process commonly called medieval pigment without using molten salts has long been used as a method for coloring the glass [18-20]. The method is favored for its simplicity and its practice in the field of manufacture of glasses doped with silver. In this process of coloration, silver clay composed of a mixture of silver salt, clay or ocher, water and Arabic adhesive is applied on the glass surface. Afterwards, the painted glass was submitted to the heat-treatment to obtain the color [21, 22].

Compared with ion exchange method using molten salts, staining with medieval painting process has significant advantages including low cost and versatility, without limitation, glass shapes [20]. Few studies have investigated the staining method [23-25] unlike those who were interested to the process of glasses immersion into molten salt solution [25-27]. The effect of different component types of Silver used in the silver clay for coloring glasses by the medieval pigments method was

investigated by Jembrish-Simburger et al. [24]. Pérez-Villar et al. [22] investigated the effect of the clays types utilized in the stain. It was shown that the properties of clays such as specific surface, porous volume and iron concentration (Fe_2O_3) are important factors that influence the yellow coloration.

In this work, the medieval staining process was used for the coloration of two glasses types, the soda-lime and the borosilicate glasses. Moreover, a parametric study was conducted for the purpose to determine the influence of the concentration of silver clay and heat treatment duration on the glasses coloration and the engendered structural changes. Characterization of the composition and structure of silver doped glasses is performed by UV-Visible Spectroscopy, Abbe Refractometer and the Scanning Electron Microscope where the EDX technique was used to determine the penetration of Silver into glass. The last found results were compared with those obtained by confocal Raman spectroscopy.

EXPERIMENTAL

Samples preparation

Two types of glasses have been used in this study: the soda-lime and the borosilicate. Their chemical compositions presented in Table 1 were determined by X-ray fluorescence technique and by the bolometric method, for the soda-lime and the borosilicate glasses respectively. The mean size of the used samples is $30 \times 30 \text{ mm}^2$, thickness about 5mm for the soda lime and 1.1 mm for the borosilicate. A silver stain was prepared and spread on the surface of the two types of glasses using a small brush. Only one side surface of glass has been painted. The silver clay was prepared in two concentrations: C1: 15 mg of AgNO_3 , 45 mg of kaolin, 3 drops of Arabic adhesive for each sample. C2: 8 mg of AgNO_3 , 30 mg of kaolin, 3 drops of Arabic adhesive for each sample.

Ten samples were prepared for each concentration (five for each kind of glass). The painted samples were heat treated to obtain the silver diffusion into the glass structure and the development of the yellow color. This was achieved by heating the samples in air at 580°C and 600°C for the soda-lime and the borosilicate glass respectively, for different a periods of time varying from 2 hours for the first sample to 6 hours for the fifth one. The heating rate was $2^\circ\text{C}/\text{min}$, and the cooling rate was $1^\circ\text{C}/\text{min}$. At the end, the silvered glasses were washed with distilled water to remove traces of stain residual.

The prepared samples are identified by a letter indicating the kind of glass (S for the soda-lime glass and B for the borosilicate glass) followed by two numbers indicating respectively the concentration of silver clay and time at the maximum temperature. For example, the sample B12 represents the borosilicate glass sample which was painted using the silver clay prepared with the concentration C1 and heat treated for 2 hours.

Characterization techniques

The optical transmission spectra of prepared samples were measured using a UV-Vis Spectrophotometer (Perkin-Elmer Lambda 40) and a flat soda glass used as a reference. Measurements were performed at room temperature in the wavelengths range of 300 to 1100 nm. The color parameters were calculated from the transmission spectra using the standards of the International Commission of Luminance (CIE) L^* , a^* , b^* [27]. A scanning electron microscope coupled with X-ray microanalyser was used to identify and quantify the chemical elements present on the surface cut crosswise of the silvered glasses thereby determining the diffusion depth of the silver nanoparticles in the treated glasses. The typical accuracy of measurements by X-ray is approximately 2 %.

Complementary tests were performed using the Raman confocal spectroscopy technique to determine the penetration depth of the silver in the painted glass and to compare the results with those found by the EDX technique. The Raman confocal spectroscopy tests were performed using a 514.5 nm Ar + laser, its intensity was fixed to 2.5mW and the exposure time was 10s, the accumulation number was 50. Measurements were made at room temperature in the range of analyzed frequencies varying between 1300 and 100 cm^{-1} using an objective ($\times 100$) with $5 \mu\text{m}$ of the penetration step. Finally, the Abbe Refractometer was used to study the refractive index variation of the painted glasses according to the silver clay concentrations and the heat treatments.

RESULTS

Absorption spectrum of UV-Visible

Figure 1 presents the UV-Visible absorption spectra of the studied glasses. Contrary to the raw glasses (S0, B0), it is to be noted that the painted glasses present

Table 1. Chemical composition of the studied glasses.

Content (wt.%)	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	B_2O_3	Others*
Soda lime	72.40	1.26	13.40	0.24	8.53	3.95	0.16	–	0.06
Borosilicate	80.50	2.49	3.60	0.66	0.21	0.14	0.20	12.10	0.10

* Others: P_2O_5 , TiO_2 , ZrO_2 ...

an apparent absorption in the visible light characterized by the appearance of an absorption peak at the same wavelength of 420 nm. It was remarked on the Figure 1 that the absorption peak is more intense as the concentration of spread silver clay on glasses and/or heat treatment duration increases. Indeed, it is observed in the Figure 2a that the absorption of glasses S13, S14, S15, S16 doped with silver at higher concentration and heat treated for 3, 4, 5 and 6 hours respectively is maximum (100 %) at the wavelength of 420 nm, and it is around 97 % for glass S12 heat treated for 2 hours. The same tendency was observed in the case of the borosilicate glass (Figure 2b), except for the B12 glass.

Using an appropriate program, we determined the color factors, from the absorption spectra of UV-Visible. Table 2 shows the dependence of these concentration factors and/or heat treatment duration on the studied glasses. It was obtained surfaces colored from the light yellow to the amber. For the same heat treatment time, it is observed that the color is more intense on glasses doped with silver clay at high concentration (C1) (see Figure 1). Furthermore, for the same concentration the color is more intense on glasses treated for longer times (see Figure 2).

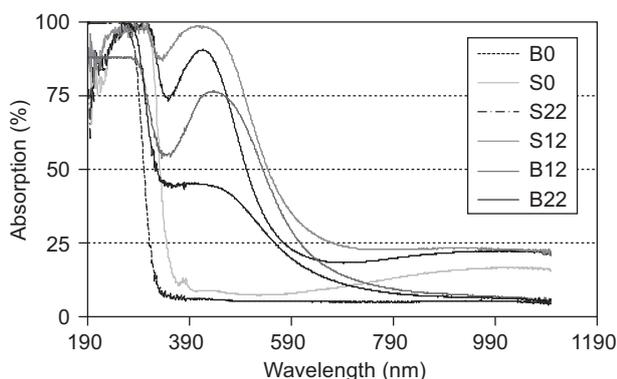


Figure 1. UV-Vis absorption spectra of the silver-stained soda-lime and borosilicate glasses.

It was noted that the luminosity factor (L) of glasses decreases of the values 96.6 and 95.32 for soda-lime and borosilicate raw glasses respectively, whereas it decreases of the values 71.5 and 73.2 for the S15 and B16 painted glasses respectively.

By inspecting the Table 2 and the Figure 3 it is seen clearly that the obtained color factors indicate an evident color change with the concentration and painted glass type and less obvious with the heat treatment time. Additionally, the factor (b) tends to be constant since four hours of heat treatment.

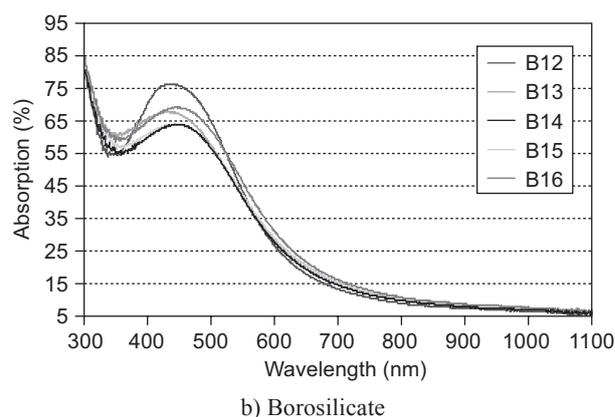
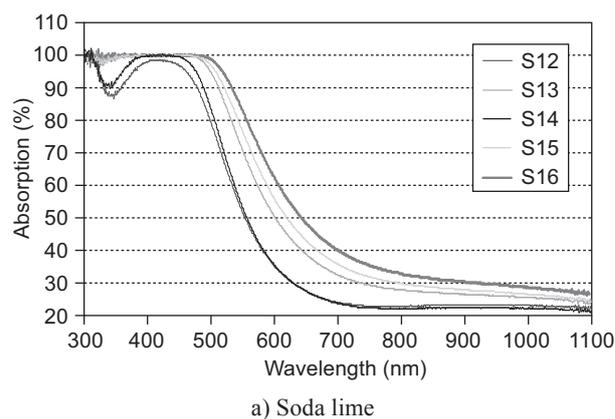


Figure 2. UV-Vis absorption spectra of the silver-stained glasses painted with different time of thermal treatment.

Table 2. Optical aspect and chromatic coordinates of painted glasses.

	S12	S13	S14	S15	S16	S22	S23	S24	S25	S26
L*	76.5 ± 0.2	74.60 ± 0.1	73.20 ± 0.07	71.5 ± 0.1	87.65 ± 0.08	89.8 ± 0.2	85.6 ± 0.2	83.45 ± 0.04	83.05 ± 0.08	83.1 ± 0.1
a*	21 ± 1	19 ± 1	24 ± 2	20 ± 1	22 ± 2	-7.3 ± 0.2	-7.4 ± 0.2	-7 ± 1	-6.9 ± 0.7	-6.5 ± 0.7
b*	50 ± 2	52 ± 2	55 ± 1	55 ± 2	56 ± 1	40 ± 2	43 ± 2	48 ± 1	48 ± 1	48 ± 3
Co- lor	Amber	Amber	Amber strongly	Amber strongly	Amber strongly	Light yellow	Light yellow	Light yellow	Light yellow	Light yellow
	B12	B13	B14	B15	B16	B22	B23	B24	B25	B26
L*	74.6 ± 0.7	73.4 ± 0.3	75.3 ± 0.5	74.4 ± 0.9	73.2 ± 0.9	84.6 ± 0.3	83.1 ± 0.7	81 ± 1	80 ± 1	79 ± 1
a*	7.5 ± 0.7	7 ± 1	7.3 ± 0.2	7 ± 1	8.3 ± 0.7	6.3 ± 0.7	6 ± 2	6.9 ± 0.2	7 ± 1	6.5 ± 0.2
b*	25 ± 1	26 ± 1	25 ± 1	25 ± 1	25.4 ± 0.9	20.3 ± 0.6	21.3 ± 0.5	22 ± 2	22.4 ± 0.9	22 ± 1
Co- lor	Amber	Amber	Amber	Amber	Amber	Light yellow	Light yellow	Light yellow	Light yellow	Light yellow

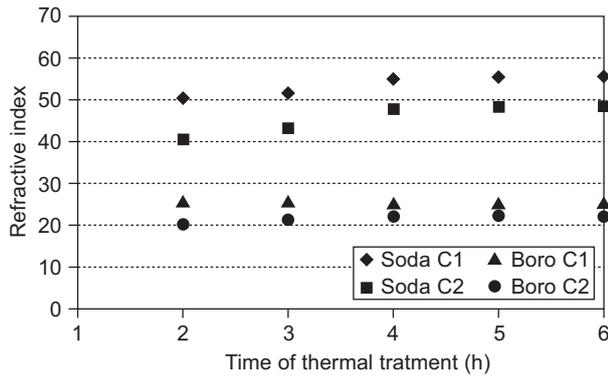


Figure 3. b^* color coordinate of stained glasses vs. heat treatment duration and stain concentration.

Silver diffusion in the glass

Using the EDX technique, the penetration depth of the silver in the stained glasses was determined. Figure 4 illustrates the variations of the proportions of silver atoms and ions versus the penetration depth into the glass. A note that this analysis technique is not sensitive to the chemical states of silver [20].

In Figure 4, it is to be observed that the silver diffusion in soda-lime glass was greater than that in the borosilicate glass. In fact, it is seen in the results that the silver penetration depth into the glass S12 is about 150 μm while for the B12 glass is about 70 μm for the same silver concentration which is 1%. In addition, the silver diffusion is more important as the silver concentration in the stain increases.

Figure 5 shows that the silver diffusion inside the soda lime glass is best for the samples that undergo longer heat treatment.

However, in Figure 6 it can be observed that the sodium and silver behaviors are opposed. Indeed, sodium concentration starts low close the glass surface about 8% for the S12 glass and 1.9% for the B12 one and increases to reaches a constant values about 11% and 3% respectively for the two glasses, thus showing that in this depth there is no ionic exchange.

The SEM micrographs in Figure 7 of the S12 glass show the formation of silver nanoparticles and clusters and their concentrations at three different points in the glass structure: 20 μm , 60 μm and 100 μm from the glass surface.

These micrographs show the presence of silver nanoparticles in the glass structure, which tend to agglomerate to form clusters distributed in a not homogeneous manner. We also note by comparing Figure 7 the concentration of silver nanoparticles and clusters decreases with distance from the surface.

The silver diffusion in the glasses was also studied by Raman confocal spectroscopy. Figure 8 compares the curves registered during the penetration into the glass S12 and S0 (unpainted glass). The penetration depth for which it was found that the registered curve is similar with the original one (absence of peak located at 210 nm)

is the limit depth of the silver diffusion into the glass. It was found for the soda lime glass (S12) a diffusion depth around 165 μm and about 35 μm for the borosilicate glass. Figure 9 shows that the measured refractive index of the painted glasses changes with the silver concentration in the glass, and this change is less obvious versus the heat treatment duration where a tendency of constancy of the index for both glass kinds.

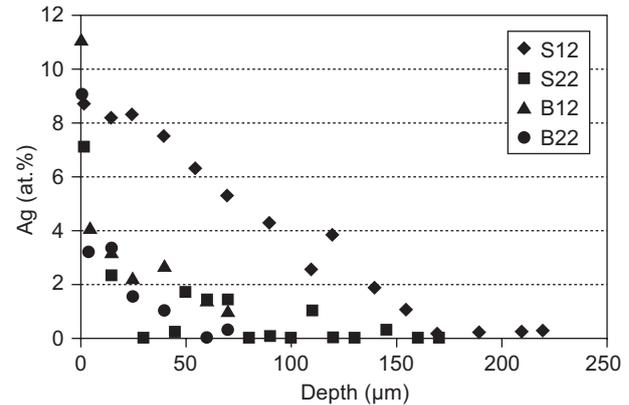


Figure 4. Concentration profiles of Ag in silver-stained glasses for several mixture concentrations.

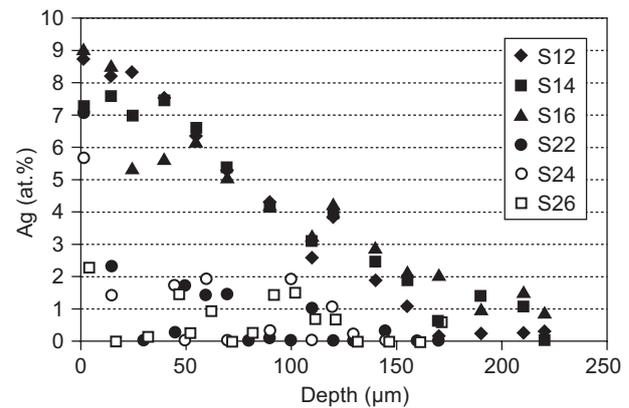


Figure 5. Concentration profiles of Ag in silver-stained soda lime glass vs. heat treatment duration and stain concentration.

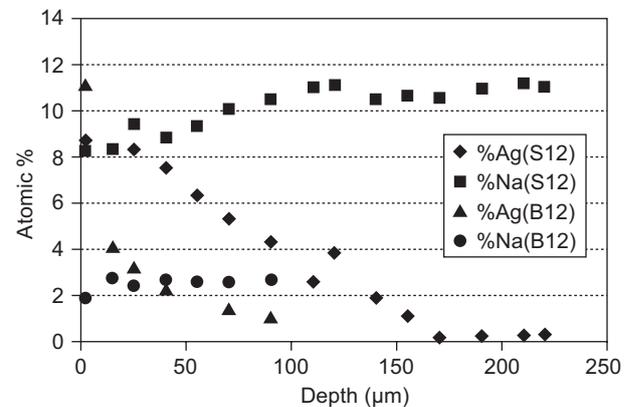


Figure 6. Variation of silver and sodium concentration in deep of the glass.

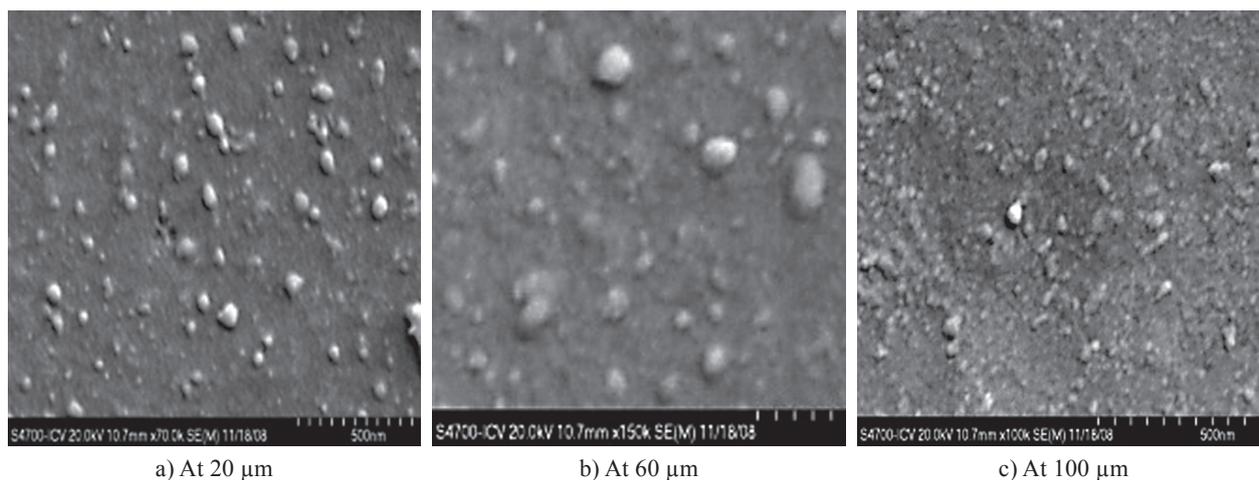


Figure 7. SEM Micrographics obtained after ion-exchanged process for the soda lime glasses.

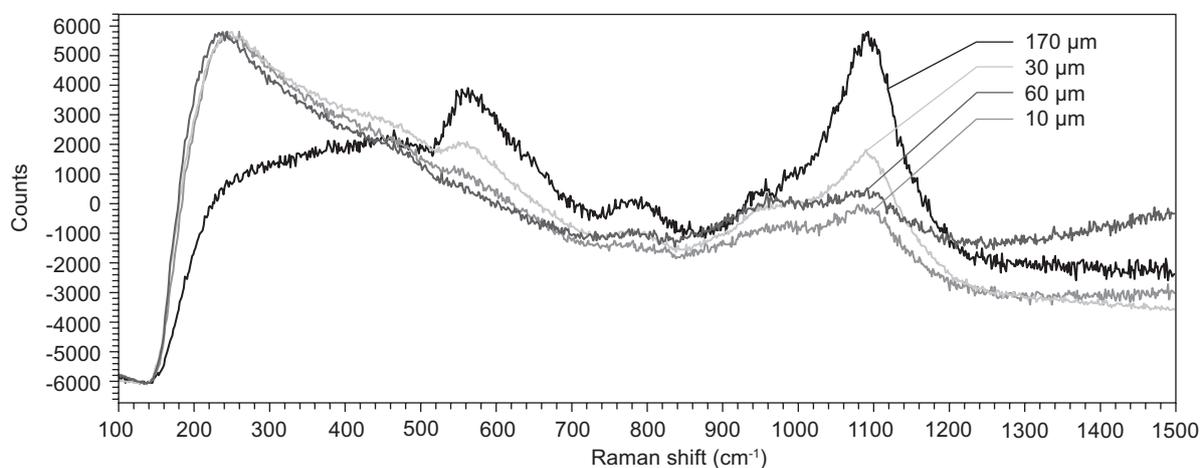


Figure 8. Confocal Raman spectra of silver-stained soda lime glasses in deep of the glass.

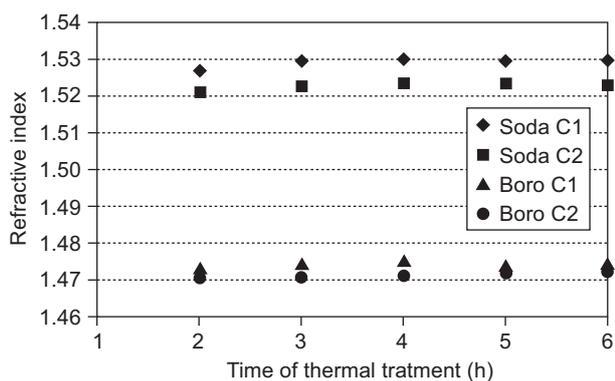


Figure 9. Variation of refractive index versus heat treatment duration and stain concentration.

DISCUSSION

The color of the glass surface presented in Table 2 is due to the formation of silver nanoparticles. The increasing of the color intensity is caused by the clusters size growth or increases of their concentration, which was confirmed in the study [20].

Formation of Ag^0 aggregate gives a yellow color to glass; this shows that the optical absorption spectrum has reached a peak around 420 nm due to surface plasma resonance (SPR).

The intensity and position of this peak depends on the silver concentration diffused into the glass and the size of silver nanoparticles, the results are in agreement with those found in the study [28]. The nanoparticle radius R can be calculated according to Doyle [22, 29] from the absorption spectra shown in Figure 1 and 2 using Equation (1).

$$R_d = \frac{V_f \lambda_p^2}{2\pi c \Delta\lambda} \quad (1)$$

where; V_f is the Fermi velocity of the electron in bulk metal (silver = $1.39 \times 10^8 \text{ cm s}^{-1}$). $\Delta\lambda$ is the full width at half maximum (FWHM) of the absorption band and it is related with the size of nano clusters, and λ_p is the characteristic wavelength at which surface plasmon resonance (SPR) occurs, both determined from an optical absorption spectrum. C is the light speed ($3 \times 10^8 \text{ m s}^{-1}$).

Based on this formula and Gaussian approximations of absorption spectrum (Figure 1), the found radius of silver nanoparticles in the stained glass varies from 1.58 nm to 1.89 nm for S22 and S12 glasses respectively and it is about 1.36 nm for the borosilicate glass stained with a high concentration (B12). However, in the case of the borosilicate glass stained with the low concentration (B22), the peak is large which is reflected by a very clear color on the glass. This shows the absence of silver nanoparticles formation and the existence of the introduction of silver ions in the glass.

Still based on the Equation (1) and using the Gaussian approximation of the absorption spectra shown in Figure 2a, the mean radius of silver nanoparticles in stained glass has been calculated, we find that for samples S12, S13 respectively the radius R_d increases from 1.89nm to 1.95nm. For borosilicate glasses and using the spectra shown in Figure 2b, we found that the calculated average value of the radius R_d increases from 1.42nm to 1.61nm. The results demonstrated that increasing of the heat treatment duration causes an increase in the silver nanoclusters volume, this is more apparent on the samples S14, S15, S16.

The color of stained glasses is obtained due to the ionic exchange where the silver ions Ag^+ diffuse into the glass structure and replace the alkali ions Na^+ , which disseminate outside to the stained glass surface. According to the obtained results and those of the previous works [26,31,32], the ionic exchange is carried out as follows: At first, during the penetration of silver ions in the glass they replace Na^+ and create a liaison $Na-O-Ag$ and the remaining Na^+ ions are replaced by Ag leading to $Ag-O-Ag$ bond.

By comparison of the chemical composition of both types of studied glasses, it was found that the percentage of Na_2O is reduced in the borosilicate glasses compared to that in soda-lime glass, respectively 3.60% and 13.4%, which may explain the fact that borosilicate glass is less obvious with the ionic exchange process. This is reflected by:

- 1) The silver diffusion depth
- 2) The diameter of the formed clusters
- 3) The color intensity that is less compared with this of the stained soda-lime glass.

The study of the concentration and the heat treatment duration effects allows speculating that the effect of heat treatment duration is limited, especially after 3 hours, where there are practically color and ionic exchange saturation resulted in a constancy on the color factor curves (b^*), the refractive index (n) and the silver diffusion depth.

CONCLUSION

To enhance understanding of the effect of the silver diffusion in glasses, absorption of two types of glasses stained with the conventional method was investigated. Focusing on the effect of several parameters as the stain spread on the glass, the heat treatment duration and the glasses chemical composition on the coloration, on the silver diffusion depth and on the size of silver nanoparticles formed in the glass structure, the following conclusions were drawn: The diffusion and size of silver nanoparticles formed in the glass is less important in the borosilicate glass than in the soda-lime. This is due to the high content of alkali in soda-lime glass which favors ionic exchange in this last and therefore more intense color on stained soda-lime glasses is obtained. The heat treatment performed on both types of glass produces a bulge in the size of silver nanoparticles formed and influence slightly the silver diffusion depth in the glass. This effect is more evident for high concentrations of silver in the spread stain.

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