Coloration and structure behavior after silver and copper nanoparticles formation in soda lime glass

Farb- und Strukturverhalten von Kalk-Natron-Glas nach der Bildung von Silber- und Kupfernanoartikeln

A. Chorfa^{1,2}, N. Belkhir¹, A. Belbali¹, F. Rubio³, J. Rubio³

In this work, an ion exchange non-conventional process commonly called ancient painting process without using molten salts is used as a method for glass coloring. In this process of coloration, a mixture of metallic particles with kaolin and arabic adhesive is applied on the soda lime glass surface. Afterwards, the painted glass is submitted to the heat treatment to obtain the color. A comparative study is carried out in order to investigate the diffusion of metallic nanoparticles (silver and copper) in soda lime glasses depending on several parameters as the concentration and composition of stain spread on glass, and the heat treatment temperature. Characterization of the composition and structure of the painted glasses is performed by UV-visible spectroscopy. In addition, nanoindentation and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDS) techniques are used to determine the penetration of metallic nanoparticles into glass. The obtained result shows that the coloration of painted glass differs and depends on the concentration and the kind of the mixture of the paw. Moreover, it was found that the effect of the heat treatment temperature is primordial on the formation and diffusion of metallic nanoparticles.

Keywords: Metallic nanoparticles / glass / ion exchange / spectroscopy

Schlüsselwörter: Metallische Nanopartikel / Glas / Ionenaustausch / Spektroskopie

1 Introduction

Metallic nanoparticles are indeed tools tailored not only by their easy synthesis but also by their large capacity functionalizing surface [1]. However, the glasses containing metallic nanoparticles have attracted great interest and research especially in the last years due to their large application in: Photonics for their linear and non-

linear optical properties, biomedical, biological, and decoration [2-7]. Introducing silver and copper nanoparticles into glasses has been used for coloring glasses and recently for fabricating optical devices [8]. It has been used for decorative purposes for a very long time because of its colors, which can be yellow or orange, red or amber, due to the scattered particles of cuprous or cupric oxides as well as copper or silver metallic

¹ Institute of optics and precision mechanics, Ferhat Abbas Sétif University, El Bez Campus, SÉTIF 19000, ALGERIA

² Research Unit, emerging materials, Ferhat Abbas Sétif University, El Bez Campus, SÉTIF 19000, ALGERIA

³ Glass and ceramic institute (icv) CSIC, Campus de Cantoblanco, 28049 MADRID, SPAIN

Corresponding author: N. Belkhir, Institute of optics and precision mechanics, Ferhat Abbas Sétif University, El Bez Campus, SÉTIF 19000, ALGERIA, E-Mail: belkhir_nabil@univ-setif.dz

nanoclusters. In the last few years, these glasses have attracted attention for the blue-green luminescence properties of copper-glasses, useful for laser technology [9]. An enormous interest has grown in the development of new preparation methods of these metal nanoclusters composite glasses. Such glasses have been recently prepared by ion implantation, radiation using laser, X-ray, or γ -ray, and sol gel technique [10–12]. However, the mainly used method is still the ion exchange, which provides an easy and efficient formation of metallic nanoparticles in glasses structure [13]. The ion exchange process in soda lime glass has generated considerable interest, by its consideration as a prime technique for integrated optical device applications. In addition, it is one of the simplest and most effective methods of making optical waveguides and gradient index lenses in glasses [14].

For glasses coloration, artists have used another process, which is the classic staining method [15–17]. It is a non-conventional method where the ion exchange is accomplished without molten salts use. It is applied on the glasses surface, where the metallic element is mixed with ocher and clay then diluted with various organic carriers (glue, wine vinegar, spirit of wine, etc.) that act as binders [15].

In a previous work, this technique was used for the staining of two types of glass, soda lime and borosilicate glass [18]. It has been shown that the distribution and size of the silver nanoparticles, formed in borosilicate glass, are less important than those formed in soda lime glass. This was due to the presence of high levels of alkaline in it and the length of the heat treatment, which affect slightly the silver depth distribution. Nevertheless, they affect the size of formed nanoparticles and therefore affect the color of painted glass.

In this work, the classic method was used for the staining of soda lime glass by unary or sequential ion exchange (silver-copper and copper-silver). The objective is to clarify the influence of the complex mechanism of coloration generated by the formation of copper and silver nanoparticles on changing the structure of painted glass.

2 Experimental study

The studied glass is a soda lime glass whose composition was determined by X-ray fluorescence technique, *Table 1*. Transition temperature (T_g) of the used glass obtained by differential thermal analysis (DTA) is about 595 °C.

The used samples were of parallelepiped shape with dimensions of 30 mm $\times$ 30 mm $\times$ 5 mm (length $\times$ width $\times$ thickness). A copper and silver stain was prepared, and spread on the surface of soda lime glasses using a small brush. For each sample, the mixture was prepared using 40 mg of kaolin, two drops of Arabic adhesive and copper nitrate, copper sulfate and silver nitrate. Three different compositions of these metallic components were used. Combinations are designed respectively by N, S and Ag and are name as follows:

1. N1/S1/Ag1: 10 mg of copper nitrate or copper sulfate or silver nitrate;
2. N2/S2/Ag2: 15 mg of copper nitrate/copper sulfate/silver nitrate;
3. N3/S3/Ag3: 20 mg of copper nitrate / copper sulfate / silver nitrate.

The substrates are then heat treated at a temperature usually lower than the glass transition temperature, in order to obtain copper/silver diffusion into the glass structure and the development of the red/yellow color [16, 17]. Thus, samples were heated in air for 2 hours at different temperatures (580 °C, 480 °C, 350 °C). The heating rate was 2 °C $\cdot$ min⁻¹, and the cooling rate was 1 °C $\cdot$ min⁻¹. At the end, the painted glasses surfaces were very well cleaned before characterization.

The optical transmission spectra of prepared samples were measured using a UV-visible spectrophotometer (Perkin-Elmer Lambda model 40) with flat soda-lime glass as a reference. Measurements were performed at room temperature in the wavelengths range of 300 nm to 1100 nm. The penetration depth of the copper and silver nanoparticles in the painted glass was determined via a field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDS) using a Hitachi S-4700 equipment working at 20 kV.

Table 1. Chemical composition of the studied glass.

Content (Wt. %)	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	Others*
Soda lime	72.40	1.26	13.40	0.24	8.53	3.95	0.16	0.06

* Others: P₂O₅, TiO₂, ZrO₂.

The equipment used for the nano indentation test (NanoTest Micro Materials Ltd) is a static system that functions with a horizontal loading mechanism. It is characterized by a loading range (0 mN - 500 mN) with a force and a displacement resolutions 0.1 mN and 0.1 nm respectively. The equipment is well protected against significant thermal drift, ambient air flow and acoustic disturbance. It is equipped with a Nano-K bench top vibration isolation platform.

3 Results

The absorption spectra of the studied glasses shows that unlike raw glass S0, the painted glasses with copper mixture have an apparent absorption in the visible range, characterized by the appearance of an absorption peak near the 570 nm wavelength. It is illustrated that the absorption peak is more intense as the concentration of the copper paste spread on the glasses is high, and the coloration of the glasses painted with the copper sulfate is more intense than those painted with copper nitrate 78 % and 52 % respectively. It is noted that the spectrum of the glass painted with copper nitrate at low concentration (N1) is characterized by the absence of a peak near the wavelength 570 nm showing the non-formation of copper nanoparticles in this glass structure, *Figure 1*.

The treatment temperature plays an important role on the transmittance of soda lime glasses. Indeed, the highest values of transmittance are obtained when glasses painted with copper nitrate or copper sulfate are

Figure 1. UV-visible absorption spectra of the copper-stained soda lime glasses treated at 580 °C, vs. stain concentration, stain composition, (S0: raw glass).

heat treated at 350 °C. No peaks are observed for this treatment temperature. However, when the heat treatment temperature is increased up to 480 °C a peak located close to 570 nm begins to appear. This peak increases its intensity when the temperature is raised up to 580 °C, *Figure 2*.

The indentation curves of painted glasses have shown that the maximum penetration depth of painted glasses with copper sulfate (S3) is higher than that of glasses painted with copper nitrate (N3). The latter exhibit a similar behavior as the raw glasses (S0), *Figure 3*.

Furthermore, the slope of the unloading beginning of the indentation curve, characterizing the elastic modulus of the studied glasses, depends on the spread paste composition [19]. This reflects the elastic modulus found about 78.43 GPa, 76.33 GPa,

Figure 2. UV-visible transmission spectra of the copper-stained soda lime glasses, vs. heat treatment temperature and stain concentration, a) copper nitrate stain, b) copper sulfate stain.

Figure 3. Indentation load-displacement curve for stained soda lime glass (S3, N3) and raw glass (S0).

75.69 GPa, for the raw glass (S0), copper nitrate-glass (N3), and copper sulfate-glass (S3) respectively. This indicates that the copper nanoparticles diffusion in the glass reduces its stiffness.

Glasses painted with silver nitrate presented a more intense absorption than glasses painted with copper nitrate. On the other hand, silver glass (Ag3) present an absorption peak located at 420 nm while that of copper nitrate glass (N3) is at 570 nm. This difference in absorption indicates that greater opacity is obtained for silver glasses than for copper ones, *Figure 4*.

The diffusion of silver into the soda lime glass is greater than copper sulfate and copper nitrate, *Fig-*

Figure 4. UV-visible absorption spectra of stained soda lime glasses vs. kind of stain (silver nitrate Ag3, copper nitrate N3).

ure 5. For example, if we take a 4 μm depth penetration reference of metallic nanoparticles into the glass, it is clearly observed that the silver content in the glass Ag3 is approximately 6 % while for the same depth of penetration is about 2 % and 0.5 % of copper in glasses N3 and S3 respectively.

Nanoclusters density and volume according to the scanning electron microscope micrographs indicated a higher formation of that in soda lime glasses when silver is used, *Figure 6*. When copper is used, a few of nanoclusters are obtained. Then, it can be supposed that the structure of the soda lime glass manifests better with the formation of silver nanoparticles than with copper ones.

Sequential ion exchange glasses are characterized by absorption spectra with two peaks, *Figure 7*. The first appears at 420 nm and the second less apparent at around 570 nm corresponding respectively to the formation of silver and copper nanoparticles.

For the painted glasses color variation, it increases with the growing of the silver concentration in the

Figure 5. Concentration profiles of metallic nanoparticles in stained soda lime glass vs. stain kind.

Figure 6. Micrographics obtained by scanning electronic microscope after ion-exchanged process for the soda lime glasses, a) copper nitrate stain N3, b) copper sulfate stain S3, c) silver nitrate stain Ag3.

Figure 7. UV-visible absorption spectra of stained soda lime glasses vs. sequential ion exchange.

Figure 8. Coloration of painted glasses vs. silver concentration and heat treatment temperature.

Figure 9. Coloration of painted glasses vs. mixed composition (heat treatment temperature is 580 °C).

spread paste. In addition, opacity is observed when the treatment temperature is close to glass transition temperature (T_g). Moreover, a lack of ion exchange is observed at the treatment temperature about 350 °C and the glass remains colorless, *Figure 8*.

Moreover, colors obtained for painted glasses according to the spread paste composition demonstrate that the amber color is observed for glasses doped by silver while the red color is observed for those doped by copper, *Figure 9*. Concerning the sequential ionic exchange, the glasses react more with silver, consequently yellow and amber colorations are observed on the painted glasses.

The color parameters were calculated from the transmission spectra using the standards of the International Commission of Luminance (CIE) L^* , a^* , b^* [20].

Values of these parameters depend on the concentration and composition of the mixture and the heat treatment temperature. Some glass surfaces doped with silver were yellow to brown amber color, and others were red when they are doped with copper, *Table 2*. On other hand, it was observed that glasses painted with copper could be colored only at 580 °C. Otherwise, for the same temperature, the higher color intensity occurs for glasses doped with high concentration paste (Ag3). In summary, for the same concentration, the color is more intense when the treatment temperature is close to glass transition temperature (T_g). This confirms the existence of colorless glasses at 350 °C, *Figure 8*, *9*.

The radius of the nanoparticles “Rd” was calculated according to Doyle formula from the absorp-

Table 2. Optical appearance and chromatic factors of painted glasses*.

T	Chromatic factors	Ag3	Ag2	S3	N3	Ag3-N3	N3-Ag3
580 °C	L^*	8.43	11.81	18.58	17.03	10.40	8.16
	a^*	20.99	01.25	24.55	23.18	18.30	24.27
	b^*	27.01	20.28	18.41	17.42	24.50	26.70
Color		amber	yellow	red	red	amber	amber
480 °C	L^*	26.90	28.54	30.22	30.78		
	a^*	19.03	-1.46	-2.19	-2.02		
	b^*	27.27	12.67	4.29	2.86		
Color		amber	pale yellow	incolor	incolor		
350 °C	L^*	31.23	30.63	30.87	31.94		
	a^*	-0.89	-0.93	-0.74	-0.81		
	b^*	0.68	-0.54	-0.45	-0.27		
Color		incolor	incolor	incolor	incolor		

* L^* : brightness, a^* and b^* : color coordinates. a^* varies from negative to positive values (from green to red/magenta color). b^* varies from negative to positive values (from blue to yellow color).

tion spectra, Table 2 [21, 22]. The v_f parameter represents the velocity of the electron in the mass of metal (v_f for silver is $1.39 \times 10^8 \text{ cm s}^{-1}$ and copper is $1.57 \times 10^8 \text{ cm s}^{-1}$), Equation 1 [21, 22]. Some parameters can be obtained from the absorption spectra such: Width at half height of the absorption peak ($\Delta\lambda$) which is related to the size of nanoclusters, λ_p is the characteristic wavelength at which the surface plasmon resonance (SPR) occurs.

$$Rd = \frac{Vf\lambda p^2}{2\pi c\Delta\lambda} \quad (1)$$

Then, the absence of the absorption peak on the spectra, as in the glass painted with the lower concentration of copper nitrate or glasses treated at 350 °C produces colorless glasses. This means the absence of the metallic nanoparticles formation and only metallic ions were introduced into the glass.

The hardness values are the average of three nanoindentation tests performed on the surface of the painted glass, Table 3. The hardness of the raw glass is much higher than that of the painted glasses.

4 Discussion

The coloration of the glasses and the change of intensity are due, respectively, to the formation of the metal nanoparticles and the growth of the size and

concentration of nanoclusters [23]. The formation of silver nanoparticles (Ag^0) or copper (Cu^0), due to the surface plasmon resonance (SPR), gives respectively a yellow or red color to glasses. This is reflected by the appearance on the optical absorption spectrums of a peak around 420 nm for the silver glasses or 570 nm for the copper ones.

The intensity and position of these peaks depend on the size and the concentration of copper or silver nanoparticles diffused in the glass [24]. It is noticed that the nanoparticles and nanoclusters size depend on the heat treatment temperature and the mixture spread concentration. The shifting of the surface plasmon resonance (SPR) peaks to the lowest wavelengths (toward blue), was caused by the increase in the heat treatment temperature and the concentration of the spread paste, which induce the nanoclusters size growth.

The sequential doping silver-copper (Ag–Cu) is characterized by the formation of silver nanoparticles over those of copper, identified by the existence of a highest intensity peak around 420 nm relatively to the 570 nm one.

Otherwise, copper-silver (Cu–Ag) doping behavior is different. Indeed, during the first step of doping (copper doping), copper nanoparticles are formed and when doping silver, copper nanoclusters dissolution can take place in the same time of formation of silver which induced again peak around 420 nm more intense than the 570 nm one [25].

Table 3. Essential characteristics of painted glasses.

	Δp [nm]	$\Delta\lambda$ [nm]	Rd [nm]	Absorption [%]	H [GPa]
N1	-	-	-	20	-
N2	572	45	6.05	48	-
N3	584	33	8.61	56	6.585 ± 0.045
S1	584	40	7.10	63	-
S2	574	35	7.84	68	-
S3	569	30	8.99	78	6.410 ± 0.040
N350	-	-	-	08	-
N480	588	38	7.58	55	-
N580	584	33	8.61	56	6.580 ± 0.045
S350	-	-	-	12	-
S480	575	35	7.87	55	-
S580	569	30	8.99	78	6.410 ± 0.040
Ag3	420	29	4.48	68	6.400 ± 0.052
Ag-Cu	410/566	28/57	4.42/4.68	24/08	6.480 ± 0.062
Cu-Ag	573/410	68/32	4.02/3.80	05/17	6.560 ± 0.055
S0	-	-	-	08	6.750 ± 0.025

The shift of indentations curves for the painted and raw glasses elucidate an alteration of the painted glass structure. The observed differences are less important when glasses were treated with copper nitrate. The hardness values of painted glasses induce the thesis that their structure underwent depolymerization, leading to the destruction of silicon-oxygen (Si–O) bonds. Consequently, the hardness of painted surfaces with silver and /or copper paste decreases.

5 Conclusion

The classic staining method was used for coloration of soda lime glasses and several characterizations were done. The obtained results allow the drawing of several conclusions. The formation of nanoparticles is reflected by the apparition of an absorption band at 420 nm and 570 nm, respectively for silver and copper nanoparticles. The red color for copper and yellow or amber one for silver are obtained on the painted glasses. Annealing temperatures increase the band intensity of the absorption peak. The observed alteration of the painted glasses surfaces structure is proved by the shift between the indentation curves of the raw and painted glasses. The difference is less important in the case of glasses painted with copper nitrate. The formation and diffusion depth of silver nanoparticles is higher as those of copper nanoparticles. In summary, the studied glasses manifests better with silver nanoparticles formation and diffusion as with copper nanoparticles.

6 References

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