Modifying of Float Glass Surface with Silver Nanoparticles by Ion - Exchange

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Abstract: *In this study we treated float glass samples in melts of silver containing salts. Our aims are to study the processes of Ag nanoparticle formation in order to clarify the most likely mechanism of colour and nanostructuring processes in the modified surface layer. The UV-VIS spectra show an absorption peak around 450 nm as a prove for colloidal silver particle formation. The cut-off wavelength of the transmission varies from 400 to 520 nm. The process of particle formation is studied by SEM and XRD. The structural changes in the glassy matrix are studied using DRIFT spectroscopy. The IR spectra proof that the structure of the glasses was modified mainly by the shift of the main stretching vibration in the 1050 – 1100 cm^{-1} spectral range. The analysis of the results of spectroscopic and microscopic studies allow conclusions to be drawn on the influence of the ion exchange time (5–60 min), composition of the salt melt (1-5 mol% AgNO$_3$, 95-99 mol% NaNO$_3$) and the additional heat treatment (700 - 900°C, 60 min) on the nanoparticle sizes, optical characteristics and structural changes in the surface layer of the glasses.*

Keywords: *float glass; ion - exchange; silver; nanoparticle*

I. Introduction

Nanosized metal particles embedded in silicate glass are subject of systematic studies in relation to the widespread application of these materials for photosensitive [1, 2] and strengthened glass [3-8], as well its decoration [9-19] creating an optically inhomogeneous environment (optical devices, waveguides etc.) [20-24]. Ion - exchange is a well-known technique for fabricating of these materials. It is well known that the multicomponent oxide glasses contain glass formers and modifiers - alkali metal ions assuring the appropriate physicochemical properties. If these ions (Li, K, Na) are introduced in the glass structure during the melting process the network bonds in the emerging structure are reduced due to the increased non-bridged oxygen. This phenomenon is a prerequisite for the ion - exchange as a result of inter diffusion of an ion (A$^+$) associated with a glass matrix (X$^-$) and a required metallic ion (B$^+$) from salt bath (X$^-$A$^+$+B$^+$ $\leftrightarrow$ X$^-$B$^+$ + A$^+$) leading to changes in the color, refractive index, chemical resistance, etc. The colouring of the glasses is due to the formation of metallic (Ag, Au, Cu) colloidal particles. Especially the silver ions with their ionic radius, high activity and mobility are very suitable for the ion - exchange treatment. There are a lot of literature data concerning the Ag - Na ion exchange in commercial Na - Ca silicate glasses. The silver ions are embedded in the glass surface using different mixed salts (AgNO$_3$ [2, 25, 26], AgNO$_3$ – LiNO$_3$ [2]; AgNO$_3$ – KNO$_3$ [8, 27]; AgNO$_3$ – NaNO$_3$ [28, 29, 30, 31]; AgSO$_4$ - CuSO$_4$ – Na$_2$SO$_4$ [13], AgNO$_3$ – NaNO$_3$ – CuCl [32]). In these cases the formation of colloidal silver particles is a result of a two-step ion-exchange [33], further thermal treatment [18, 24, 26, 32, 34], UV or X-ray radiation requiring higher temperatures (450-700°C) and longer treatment times (60 – 600 min.) [18, 24, 26, 32 - 35]. If glasses containing tin ions (float glasses) are used the formation of noble metal nanoparticles by ion - exchange is a result of the Ag reduction, gold or copper ions favored by low oxidation form of tin (Sn^0, Sn^{2+}) and followed deeper penetration, distribution and aggregation [12, 35 - 40]. This is a cost-effective process without additional treatment leading to higher consumption of time and energy.

This research aims to study the formation and aggregation of nanoparticles in the surface layer of ion - exchange treated float glass in melt containing silver salt in order to clarify the influence of the ion-exchange conditions (treatment time, concentration of silver ions in the composition of the melt and the additional heat treatment - temperature and gas environment) on the size of nanoparticles, the structural changes in the surface layer of the glass and optical properties of the glass.

II. Experimental

Materials and Reagents

The experiments were made on float-glass samples with composition 73SiO$_2$.13Na$_2$O. 8CaO.4MgO. 2Al$_2$O$_3$ (mol %) and size 25x20x3mm. They were treated in melts of silver containing salts with composition:

- 1 mol% AgNO$_3$: 99 mol% NaNO$_3$
- 2 mol% AgNO$_3$: 98 mol% NaNO$_3$

• 5 mol% $AgNO_3$: 95 mol% $NaNO_3$

The ion - exchange process was performed in a vertical furnace. The glass plates were immersed in molten bath in porcelain crucible. The ion - exchange treatment was carried out at temperature 400°C and the time of treatment varies from 5 to 60 min. The samples were subsequently removed from bath, cooled to room temperature, washed in water and dried. Some of the ion - exchanged samples are additionally thermally treated at 700°-900° C for 60 min.

Table 1 Composition of the melt, temperature and time of ion - exchange and additional treatment of float glass samples.

Sample	$AgNO_3$:$NaNO_3$ mol%	Ion-exchange treatment		Additional treatment	
		T (^{0}C)	τ (min)	T(^{0}C)	τ (min)
0	untreated	------------		---------	
C_2	1:99	400	10	---------	
C_4	1:99	400	45	---------	
R_2	2:98	400	10	---------	
R_4	2:98	400	45	---------	
F_1	5:95	400	5	---------	
F_{1-1}	5:95	400	5	700 (air)	60
F_{1-2}	5:95	400	5	700 (N_2)	60
F_{1-3}	5:95	400	5	900 (N_2)	60
F_2	5:95	400	10	----------	
F_3	5:95	400	20	----------	
F_4	5:95	400	45	----------	

Characterization techniques

UV-VIS spectra were recorded on UV-VISSIBLE (Cary100-Varian) spectrophotometer in the range 300-800 nm. Structural and microstructural changes of the glass matrix, proving the formation of nanocrystalline particles were studied by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT-FTIR Spectrometer MATSON 7000). The phase composition was determined by XRD, using X-ray diffractometer Philips PW 1050. The morphological peculiarities are studied by Scanning electron microscopy (SEM-JEOL 5510). The size of the particles and roughness of the surface after treatment are registered by means of AFM (Nano Scope Tapping Mode TM).

III.   Results And Discussions

The visual evaluation of the ion - exchange glass shows that regardless of the treatment, all samples have a smooth, uniformly colored brown surface without corrosion and surface clouding. Significant difference in the staining intensity was not observed with increased salt bath time.UV-VIS spectra of the ion - exchange samples depending on the time of treatment are presented in Figure 1. Sharp decreasing in the transmission of the ion - exchange samples was found in comparison to the untreated sample. The appearance of the absorption peak around 450nm is due of the Surface Plasmon Resonance (SPR) in these samples and corresponds to the brown coloring of the glass. Some authors explain this peak by the formation and aggregation of Ag particles with colloidal dimensions [12, 32, 41-43]. SPR intensity and position depend on the concentration and size of the Ag nanoparticles diffused into the glass matrix [10, 11, 32, 44]. The cut-off wavelength of the transmission of these samples shifts from 300 (for untreated sample) to 530nm depending on the concentration and size of the Ag nanoparticles diffused into the glassy matrix.
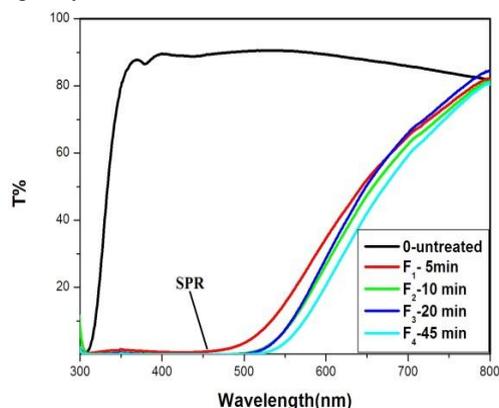

Figure 1 Transmission spectra of glasses before and after ion - exchange in a molten salt 5 $AgNO_3$ –95 $NaNO_3$ mol% for various times at 400°C.

The change in the spectra of samples treated in molten salt with different Ag - ion concentration is shown in Figure 2. Trend towards transmission decreasing (Fig. 2a) was observed at shorter time of treatment (10 min) at Ag ion increased content in the salt bath. At longer processing times (45 min) the spectra of samples treated in melts with low Ag concentration (1-2% $AgNO_3$) are similar (Fig. 2b). Transmission decreasing was found at the highest Ag concentration (5% $AgNO_3$). Regardless of the salt bath composition all samples show that the cut-off wavelength of the transmission varies from 400 to 520 nm with $AgNO_3$ increasing content. The maximum transmission at 700 nm, exceeding that one of the untreated sample was registered at lower salt bath concentration.
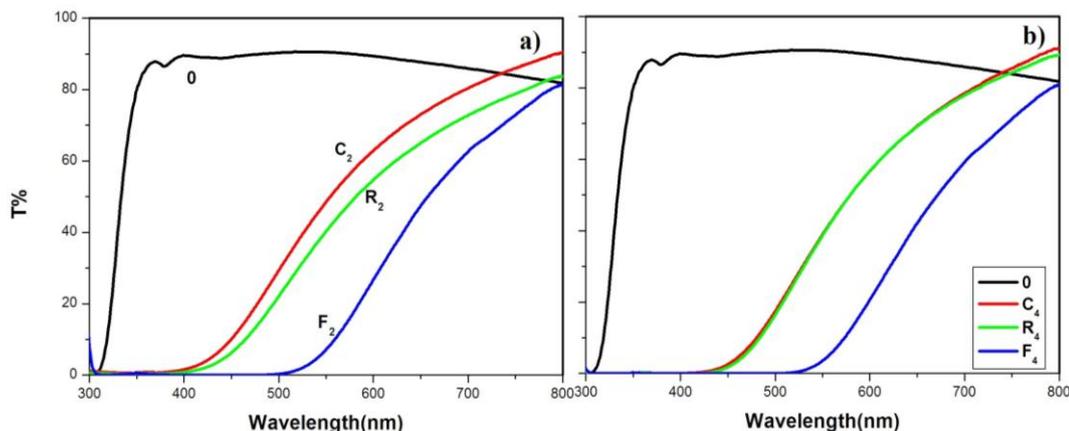

Figure 2: Transmission spectra of ion - exchange treated float glass samples at 400°C and permanently processing time - 10 min (a) and 45 min (b), depending on the melt composition - C_2, C_4 –

1 $AgNO_3$, 99 $NaNO_3$ mol%; R_2, R_4 – 2 $AgNO_3$, 98 $NaNO_3$ mol%; F_2, F_4 - 5 $AgNO_3$, 95 $NaNO_3$ mol%;The influence of the additional heat treatment at 700˚C - 900˚C, 60 min in air or inert environment on optical characteristics of the ion - exchange treated samples (400˚C, 5 min) is shown in Figure 3. For the sample additionally treated in air atmosphere at 700°C for 60 min lightening and shift of the cut-off of the transmission to shorter wavelengths (from 420nm to 380-400 nm) were observed. This could be explained by the displacement of equilibrium $Ag^+ \leftrightarrow Ag^o$ to the left [38, 45]. When the same sample is additionally treated for the same time and temperature but at different atmosphere (N_2) insignificant change of the color and lightening in 500-600 nm region was found. The transmission of the samples (F_{1-1} and F_{1-2}) above 600-650 nm is much lower than that one of the sample without additional treatment. At higher temperatures of the further processing the glass sample (F_{1-3}) becomes completely opaque with extraction shape and milky opal color. These results show that the inert atmosphere favored aggregation of the formed silver nanoparticles.
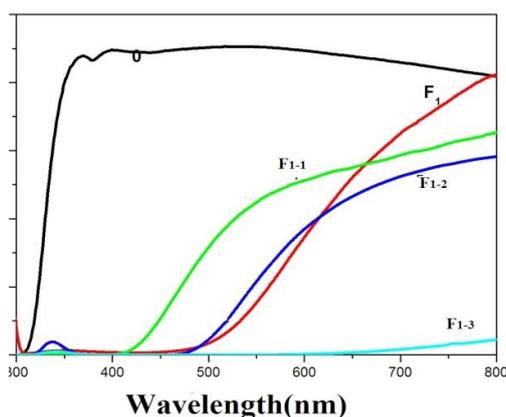

Figure 3 Transmission spectra of float glasses in dependence on the temperature and gas environmen at additional heat treatment for 60 min – F_1 and without additional treatment; F_{1-1} – 700°C, air;

F_{1-2} - 700°C, N_2; F_{1-3} - 900°C; N_2The structural changes of silicate network occurring in the glass after the ion - exchange at different conditions are shown in Figure 4 by presence of the structural units Q^n (n – number of bridging oxygen atoms) according to SiO_4 tetrahedra. On the DRIFT spectrum of before ion - exchange untreated glass present characteristic bands of Q^3 stretching at 1065 cm^{-1} and bending at 476 cm^{-1} vibrational modes of the Si - O - Si bonds. After the ion - exchange treatment the spectrum was not changed

significantly (Fig. 4a). The decreasing in the frequency of Q^3 stretching band from 1065 to 1056 cm^{-1} is taken as evidence of the increasing number of non-bridging oxygen favoring the diffusion of metal ions in the glass matrix [46]. Similarly, the shoulders of the peak at 1065 cm^{-1} corresponding to Q^2 (930 cm^{-1}) and Q^4 (1250 cm^{-1}) shifted to lower frequencies due to depolymerization processes. The red shift of the main vibrational bond could be associated with densification of glass network reflecting to the decrease in Si-O-Si bond angles [47, 48]. On the other hand, Q^3 bending band decreased also [476 → 467 cm^{-1}], which is associated with increasing of bridging oxygen atoms. This behavior could be explained with emergence of the bonds between the modifier ions and the oxygen atoms from glassy network. In support of this conclusion is the broadening of 850-1250 cm^{-1} IR region connected to replacement of Na by Ag ions [49]. It has been reported that Ag_2O is characterized by the infrared bands at 525-540 cm^{-1} [50, 51], 540 or 645 cm^{-1} and AgO with bands at 951 cm^{-1} and 986 cm^{-1} [52] corresponding to Ag-O stretching mode. In our case there are no bands at these frequencies, therefore it can be assumed that a significant amount of the penetrated silver is present in an elemental form. Probably the silver oxides are in minimal concentration due to the fast reduction of silver ions and could not be detected by the spectrometer. The presence of tin in low oxidation state in the surface layer of the float glass plays an essential role for the formation of colloidal silver particles as well for structural transformations of the glass matrix. The appearance of the weak bands around 615, 650 cm^{-1} in the spectrum of glass sample treated for short time (F_1 - 5 min), could be connected with the presence of υ(Sn-O) or υ(Sn-O-Sn) bond at 680 cm^{-1}, respectively [51, 53-57]. These bands were not observed during prolonged retention probably due to increasing amount of silver colloidal particles as a result of the oxidation of bigger quantity tin ions to Sn^{4+} with their deeper penetration compared to Sn^0, Sn^{2+}. Figure 4b shows that after the additional heat treatment at 700°C a shift of the band attributed to the stretching vibration of Si-O-Si (1065-1105cm^{-1}) related to the polymerization of glass network in a result of the formation of bridging oxygen was observed. In this case the frequencies of both vibration Si - O - Si modes are shifted towards higher values and could be explained with formation of tighter glass network or it is also possible to consider that the tin ions are able to enter into the matrix as the glass-formers [46]. Furthermore, the additional processing leads to depletion of low oxidation forms of the tin preventing the further reduction of embedded silver particles and determines the increased presence of Ag^+ ions in the surface layer of the glass and the occurrence of Ag - O bonds. In support of this conclusion is the result of UV-VIS analyses (see Fig. 3) showing crossing of silver particles from elemental in ionic state at these conditions. Therefore, it could be accepted that the band around 968 cm^{-1} corresponding to AgO, although in have been established different frequencies (at 951 cm^{-1} and 986 cm^{-1}) characterized AgO [52]. The higher temperature (900°C) also causes polymerization of glass network - Q^3 stretching band shifts from 1065 to 1076cm^{-1}.
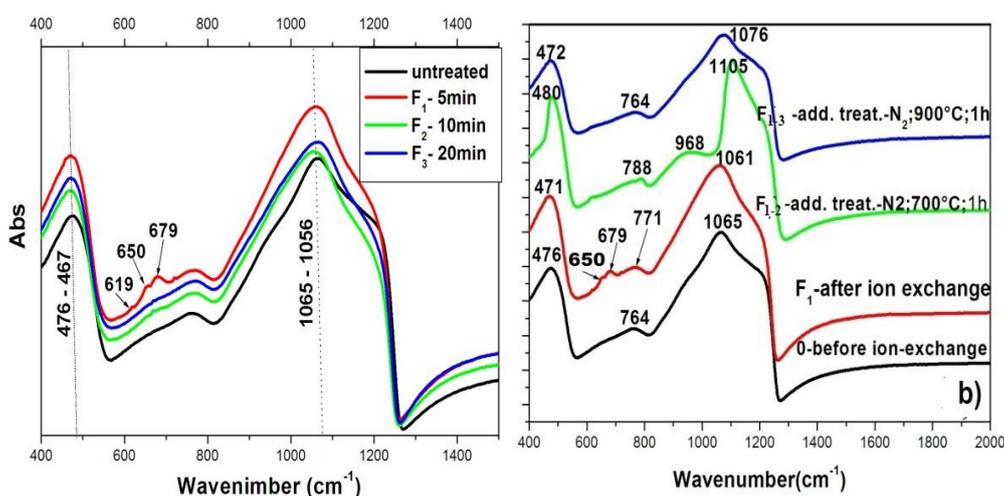

Figure 4 DRIFT spectra of float glasses treated in melt with composition 5 mol% $AgNO_3$-95 mol% $NaNO_3$ depending on: a) the time of treatment; b) the additional heat treatment

XRD pattern of the silver ion-exchanged sample (F_4) is shown in Figure 5. Diffraction peaks were appeared at 2θ position 38, 12˚; 44, 31˚ and 64, 45˚ corresponding to (111), (200) and (220) planes of silver alone has proved that the formed nanoparticles are elemental silver.
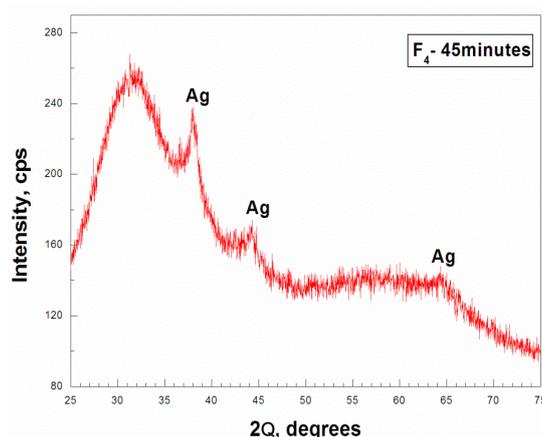
Figure 5 XRD pattern of F_4 sample ion - exchange treated at 400°C for 45 min.

SEM micrographs confirmed the presenting results (Fig. 6). The images show presence of nanocrystalline particles with spherical shape and size ranging from 15 to 100 nm. The increasing of the nanoparticles to 200 - 250 nm was observed after additional heat treatment. The higher temperature (900˚C) leads to the formation of surface crystallized layers, their phase separation and observed plate-like crystal morphology.
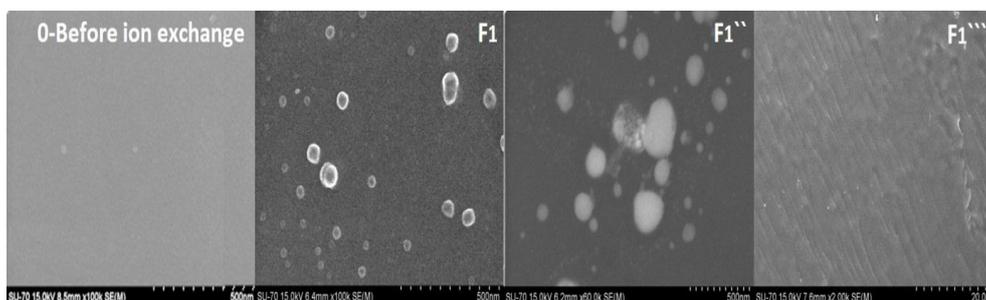

Figure 6 SEM micrographs of float glasses before (0) and after (F_1) ion - exchange in melt with composition 5 mol% $AgNO_3$, 95 mol% $NaNO_3$ and after additional heat treatment for 60 min at temperatures 700°C (F_{1-2})and 900°C (F_{1-3})

Three-dimensional AFM images present the topography of an ion - exchange sample (F_1). The analysis shows the roughness of the background surface around 10-12 nm and the size of the formed nanoparticles are in the range of ~15 nm (Fig. 7).
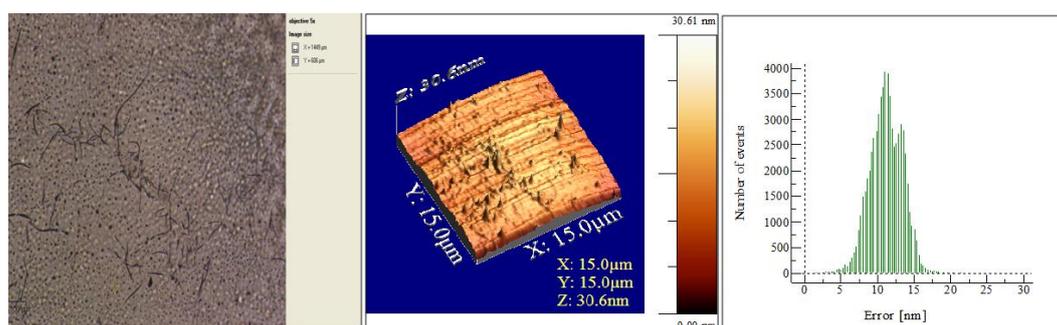

Figure 7 AFM images of surface of ion - exchange sample F_1 with embedded Ag nanoparticles around 15 nm.

The experimental data show significant changes in the optical properties of ion - exchange glasses treated in silver containing melts. The observed absorption peak around 450 nm was associated with the formation of Ag colloidal nanoparticles in the surface layer of the glass and explained staining in brown. A high content of Na_2O in the composition of the float-glass is essential for the larger number of nanoparticles, their deeper penetration, formation of clusters and the significant intensity of coloring [44, 58]. The size of formed silver nanoparticles from 20 to 250 nm is established on the basis of SEM analysis. The evaluation of the absorption and the particle size was provided by investigation of the SPR band via Mie simulation (Fig. 8). It has been found that particles with size 20 nm exhibit only absorption caused by the dipole oscillations of the

conduction electrons and narrow SPR is appearance. While the presence of larger nanoparticles with size 50 nm or 150 nm is a reason for equal absorption and scattering or attenuation of the absorption, respectively (Fig. 8a). This phenomenon explains the limited transmission due to non-uniform electromagnetic field across the particles causing excitation of multiple resonances (eg. quadruple) and flat UV-VIS spectra [17, 59]. Therefore, the cut-off wavelength of the transmission of the ion - exchange treated sample can be associated with the formation of particles greater than 50 nm. The formed larger particles and the predominance of particles with a size around 50 nm in our sample (e.g. F_1) are responsible for emergence of absorption peak namely around 450 nm. The absorption spectra of the formed particles according to size were compared in Figure 8b. It is obvious a red shift with increasing the particle size to 50 nm. The occurrence of two peaks in the absorption spectra of particles with a size 100 - 150 nm as a result of multiple resonances can be associated with the displacement of cut-off wavelength of the transmission to higher frequencies, if optical characteristics are presented in a transmission. Its shifting to the right is an evidence for the raising of the concentration and particle size also of their deeper penetration leading to an intensification of the colour intensity of the glass samples [10, 44, 45, 60]. Furthermore, the red shift can be associated with an increase of the refractive index [61].
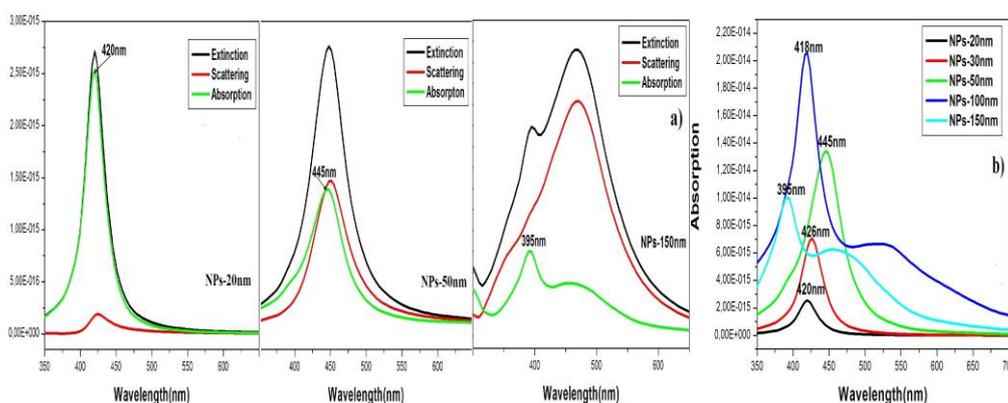

Figure 8 Optical properties of silver nanoparticles determined by Mie simulation

DRIFT spectroscopy study of Ag/Na ion-exchange has shown that replacement of Na^+ by Ag^+ modifier ions induces structural changes in the glass network. It is known that the tin formed a hump in the surface layer of float glass, preventing deeper penetration of modifying ions [12]. This phenomenon is related to the presence of iron oxides in the composition of the glass ($Fe^{3+} + Sn^{2+} \rightarrow Fe^{2+} + Sn^{4+}$). The oxidation is carried out near the surface and limited the penetration of modifier ions. In the composition of our samples Fe^{3+} ions are not present, consequently in the tin profile could not be observed the presence of a satellite peak resulting of accumulation of Sn^{4+} [62, 63]. Thus is carried out an unobstructed diffusion of Ag^+. This condition allows a deeper penetration of silver ions determining the high intensity of the colouring, chemical and mechanical resistance [64]. In this case the cumulative effect of Sn^{4+} will appear only after the penetration of Ag^+ ions oxidized Sn^{2+} inducing structural changes in the surface layer. This was established with the appearance of bands in the IR spectra corresponding to the Sn - O bond. However, SnO_2 in the glass surface leads to decreasing the number of bridging oxygen atoms and increasing the number of non-bridging ones favoring ion - exchange process [47, 65]. The concentration of tin ions in depth is higher and additional heat treatment allows their incorporation as glass formers as evidenced by the blue shift of Q^3 stretching band. The higher temperature (900°C) leads to aggregation of Ag nanoparticles and formation of crystallized layers.

These results confirm the data obtained by other authors [58, 66], concerning an ion exchange mechanism:

- Diffusion of silver ions in the glass matrix replacing Na^+ ions.
- Reduction of Ag^+ to Ag^0 favored by the presence of low oxidation form of the tin ions (Sn^0 and Sn^{2+}) located in the surface layer of glass [62, 67];

Silver colloidal particles show interesting optical properties. The induced deformation changes in the microstructure of the glass matrix can provide an UV protection, a high transmission in the near IR region and effective structural changes in the light-sensitive properties, which in turn may lead to their use for new applications.

IV.   Conclusions

From conducted experimental work and the analysis of the optical and structural properties of ion - exchange glasses can be summarized the following conclusions:The treated samples are colouring in brown in a result of $Na^+ \leftrightarrow Ag^+$ ion - exchange and the reduction of Ag ions, favoured by the presence of tin ions in glass surface. With increasing the ion - exchange time the transmission of treated glasses in the visible range significantly decreases and the cut-off wavelength of the transmission shifts from 300 to 520nm. Absorption

peak around 450 nm on the UV-VIS spectra of these glasses was registered and proving the formation of silver colloidal nanoparticles as a reason for the colouring. The roughness of the background structure is 10-12 nm and the size of the nanoparticles varies from 15 to 200 nm.The concentration of silver ions in the salt bath at an operating temperature 400°C affects the staining intensity, size and quantity of silver nanoparticles in the surface layer of the float glass in dependence of the prolonged processing time. Significant influence over these processes provided additional heat treatment. This treatment provokes structural and morphological changes of ion - exchange float glasses depending on the temperature, the time of additional treatment and the gas environment. It was found the important role of tin ions for structural transformations of float glasses and crystallization processes proceeding in the glass surface. Variation in the frequencies of the characteristic bands of SiO_4 vibration units in the glass structure is evidence for polymerization changes of the silicate network.

References

[1]   H. Garfinkel, Photochromic glass by silver ion exchange, *Appl. Optics 7, 5,* 1968.
[2]   Che - Kuang W., Method of making photosensitive colored glasses exhibiting alterable photo-anisotropic effects, *US Patent*, 1980, 4191547.
[3]   S. S. Kistler*, Stresses in glass produced by nonuniform exchange of monovalent ions, J. Amer. Ceram. Soc., 45, 2,* 1962, 59-68.
[4]   Nordberg M. E., Mochel E. L., Garfinkel H. M., Olcott J. S., Strengthening by Ion Exchange, *J. Amer. Ceram. Soc., 47,* 1964, 215 – 219.
[5]   A. Bankov, Y. Dimitriev, Y. Ivanova, E. Gatev, L. Ivanova., Chemical strengthening of lens for spectacles, *J. Stroit. Mater.i Silikat. Prom., 3, 19,* 1980, (in Bulg.).
[6]   S. Karlsson, B. Jonson, C. Stalhandske*., The technology of chemical glass strengthening – a review, Glass Technol. Eur. J. Glass Sci. Technol. Part A 51,* 2010, 41–54.
[7]   V. M. Sglavo, A. Quaranta, V. Allodi., G. Marrioto, Analysis of the surface structure of soda lime silicate glass after chemical strengthening in different KNO_3 salt baths, *J. Non - Cryst. Solids*, *401*, 2014, 105-109.
[8]   D. Guldiren, I. Erdem, S. Aydin, Influence of silver and potassium ion exchange on physical and mechanical properties of soda lime glass, *J. Non-Cryst. Solids, 441,* 2016, 1-9.
[9]   G. H. Frishcat, Coloring of glass surfaces by ion –exchange, *J. Non-Cryst Solids, 19,* 1975, 367-368A.
[10]   Y. Dimitriev, Y. Ivanova, E. Gatev, Method for creating a colour image on glass by ion exchange, *Stroit. Mater. i silikat. Prom., 39,* 1977, 3-4 (in Bulg.).
[11]   D. G. Galimov, A. I. Neich, L. S. Semina, V. A. Juravleva, Optical spectra of borosilicate glasses colored with.colloidal particles, *Fiz. Khim. Stekla, 12 (2),* 1986, 230-234, (in Russ.).
[12]   S. Takeda, K. Yamamoto, K. Matsumoto, Coloration due to colloidal Ag particles formed in float glass, *J. Non-Cryst. Solids, 265,* 2000, 133-142.
[13]   A. Y. Zhang, T. Suetsugu, K. Kadono, Incorporation of silver into soda-lime silicate glass by a classical staining process, *J. Non-Crystal. Sol., 353,* 2007, 44-50.
[14]   J. Molera, C. Bayes, P. Roura, D. Crespo, T. Pradell, Key Parameters in the Production of Medieval Luster Colors and Shines, *J. Am. Ceram. Soc., 90 [7],* 2007, 2245-2254.
[15]   S. Perez-Villar, J. Rubio, J. L. Oteo., Study of color and structural changes in silver painted medieval glasses, *J. Non-Cryst. Solids, 354,* 2008, 1833–1844.
[16]   P. Colomban, The use of metal nanoparticles to produce yellow ,red and iridescent color from bronze age to present times in lustre pottery and glass, *J. Nano Research, 8,* 2009, 109-132.
[17]   P. C. Gutierrez, T. Pradell, J. Molera, A. D. Smith., A. Climent - Font, M. S. Tite, Color and Golden Shine of Silver Islamic Luster, *J. Am. Ceram. Soc., 93 [8],* 2010, 2320-2328.
[18]   T. Pradell, R. S. Pavlov, P.C. Gutierrez, A. Climent-Font, J. Molera, Composition, nanostructure, and optical properties of silver and silver-copper lusters, *J. Appl. Phys., 112,* 2012, 054307.
[19]   O. Véron, J. - P. Blondeau, D. Meneses, C. Vignolle, Characterization of silver or copper nanoparticles embedded in Soda-lime glass after stajning process, *Surf. & Coat. Technol., 227,* 2013, 48-57
[20]   J.-M. Lekhy, *Optical Waveguides with Copper Film Ion Exchange in Glass*, DISS. ETH №16496, Swiss Federal Institute of Technology Zurich, 2006
[21]   E. Cattaruzza, M. Mardegan, E. Trave, G. Battaglin, P. Calvelli., F. Enrichi, F. Gonella, Modifications in silver-doped silicate glass induced by ns laser beams, *Appl.Surf. Sci., 257,* 2011, 5434-5438
[22]   E. Cattaruzza, G. Battaglin, F. Gonella, A. Quaranta, G. Mariotto, C. Sada, S. Ali, Chromium doping of silicate glasses by field-assisted solid-state ion exchange, *J. Non-Cryst. Solids, 357,* 2011, 1846–1850
[23]   J.-P. Blondeau., O. Veron, Graded index wavguide elaboration by silver-sodium or silver-lithium ionic exchange for various glass compositions, *Opt. Mater., 34,* 2011, 278-286
[24]   A. Tsuboi, K. Nakamura, N. Kobayashi, A Localized Surface Plasmon Rezonance-Based Milticolor Electrochromic Device with Electrochemically Size-Controlled Silver Nanoparticles, *Adv. Mater., DOI: 10.1002/adma.201205214,* 2013,
[25]   B. Roy, H. Jain, S. Roy, D. Chakravorty, The development of nanosize silver particles in an ion exchanged silicate glass matrix, *J. Non-Cryst. Solids, 222,* 1997, 102-112
[26]   P. W. Wang, Thermal activation energy of silver in ion-exchanged soda-lime glass investigated by X-ray photoelectron spectroscopy, *Mater. Chem. and Phys., 50,* 1997, 213-218
[27]   H. Hofmeister, S. Thiel, M. Dubiel, E. Schurig, Synthesis of nanosized silver particles in ion-exchanged glass by electron beam irradiation, *Appl. Phys. Lett., 70,* 1997,
[28]   M. A. Villegas, J. M. Fernandez Navaro, S. E. Paje., J. Llopis, Optical spectroscopy of a soda lime glass exchanged with silver, *Phys. Chem. Glasses, 37 (6),* 1996, 248-53
[29]   M. Suszynska, L. Krajczyk, R. Capalletti, A. Baraldi, K. J. Berg, Microstructure and silver nanoparticles in ion-exchanged and deformed soda-lime silicate glasses, *J. Non-Cryst. Solids, 315,* 2003, 114-123.
[30]   M. Dubiel, J. Haug, H. Kruth, H. Hofmeister, K.-D Schike, Ag/Na ion exchange in soda –lime glasses and the formation of small Ag nanoparticles, *Mater. Sci. Eng. B, 149,* 2008, 146-151

[31]   F. Goutaland, E. Marin, H. Gagnarie, J. Y. Michalon, A. Boukenter, Efficient and Controllable Silver Nanoparticles in Ion-exchanged Soda-lime Glasses by Simultaneous Heat Treatment and UV Exposure, *7th symposium SiO₂ Adv. Dielectrics Related Dev.,* France, 2008, ujm-00377821, version 1, 2009,

[32]   K. Kobayashi, Optical and EPR studies on redox interaction layers of Ag+ and Cu+ ions diffusing into soda-lime glass, *Phys. Chem. Glasses, 20 (2),* 1978, 21-24.

[33]   X.C. Yang, L.L. Li, M. Huang, J.F. Zhao, J.W. Hou, In situ synthesis of Ag–Cu bimetallic nanoparticles in silicate glass by a two-step ion-exchange route, *, J. Non-Cryst. Solids, 357*, 2011, 2306–2308

[34]   R. S. Varma, D. C. Kothari, A. K. Mallik., A. Bhatnagar, D. Kanjilal, S. Santra, R. G. Thomas, R. Tewari, S. Neogy., G. K. Dey, Optical properties of ion exchanged and swift heavy ion beam treated silicate glasses, *Adv. Mater. Lett., 6 (5),* 2015, 425-431.

[35]   D. I. Lee, Y. K. Lee, H. S.Lee, Effects of silver and potassium ions on ion exchange in float glass, *J. Mater. Sci., 27,* 1992, 2908-2913

[36]   B. Z. Saggioro, E. C. Ziemth, Changes of physical properties of glass surfaces exposed to KNO₃ vapors, *J. Non-Cryst. Solids, 352,* 2006, 2783-2790.

[37]   A. Puche-Roig, V. P. Martin, S. Murcia–Maskaros, R. I. Puchades, Float glass colouring by ion-exchange, *J. Cult. Heritage, 9*, 2008, 129-133.

[38]   M. Dimitrova, Y. Ivanova, Y. Dimitriev, Ion-Exchange Colouring of Float Glasses in Vapours and Melts of Copper - Containing Salt, *J. Chem. Technol. Metall., 47, 4,* 2012, 409-414.

[39]   M. Dimitrova, Y. Ivanova, Y. Dimitriev, M. Marinova, I. M. Miranda Salvado, H. Fernandes, Formation of Copper Nanoparticles in the Surface Layer of Float Glass by Ion-exchange Technique, *Nanosci. & Nanotechnol., 13,* 2013, 51-55.

[40]   V. M. Sglavo, Chemical Strengthening of Soda Lime Silicate Float Glass: Effect of Small Differences in the KNO₃ Bath, *Inter. J. Appl. Glass Sci., 6 [1],* 72-82, 2015, DOI:10.1111/ijag.12101

[41]   S. Thomas, S. K. Nair, E. M. A. Jamal, S H Al-Harthi, M. R. Varma, M. R. Anantharaman, Size-dependent surface plasmon resonance in silver silica nanocomposites, *Nanotechnology 19[7],* 2008, 075710.

[42]   D. Manikandan, S. Mohan, P. Magudapathy, K. G. M. Nair, Irradiation induced dissolution of Cu and growth of Ag nanoclusters in Cu/Ag ion-exchanged soda-lime glass, *Nucl. Instrum and Method. in Phys. Research B, 198,* 2002, 73-76.

[43]   S. Peng, J. Mcmahon, G. Schatz, S. Gray, Y. Sun, Reversing the size-dependents of surface Plasmon resonances, *PNAS, 107[33]*, 2010, 14530-14534.

[44]   D. Manikandan, S. Mohan, P. Magudapathy, K.G.M. Nair, Blue shift of plasmon resonance in Cu and Ag ion-exchanged and annealed soda-lime glass: on optical absorption study, *Physica B 325* (2003) 86–91.

[45]   Y. Ivanova, Y. Dimitriev, P. Nichev, V. Toshev, Spectral characteristics of coloured glass after ion exchange, *Stroit. Mater. I silikat. Prom., 8, 25,* 1978, (in Bulg.).

[46]   M. Suzsynska., M. Maczka, E. Bukowska, K.J.Berg, Structure and IRR spectra of copper-exchanged soda-lime silica glass J. Phys., Conf. Ser. 249012048, 2010: doi:10.1088/1742-6596.249/1/012048.

[47]   T. Sequinel, S. Cava, J. O. Pimenta, S. A. Pianaro., S. M. Tebcherani, J. A.Varela, IR reflectance characterization of glass–ceramic films obtained by high pressure impregnation of SnO2 nanopowders on float glass", *Ceram. Inter., 37,* 2011, 1533-1536, doi: 10.1016/j.ceraint.2011.01.013.

[48]   K. Kawamura, N. Sarukura, M. Hirano, H. Hosono., Holographic encoding of fine-pitched micrograting structures in amorphous SiO₂ thin films on silicon by a single femtosecond laser pulse *Appl. Phys. Lett.,78, 8,* 2001, 1038-1040.

[49]   E. Stavrou, D. Palles, E. I. Kamitsos, A. Lipovskii, D. Tagantsev, Y. Svirko, S. Honkanen, Vibrational study of thermally ion-exchanged sodiumaluminoborosilicate glasses, *J. Non-Cryst. Solids, 401,* 2014, 232–236.

[50]   T. L. Slager., B. J. Lindgren, A. J. Mallmann, R. G. Greenler, The Infrared Spectra of the Oxides and Carbonates of Silver, *J. Phys. Chem., 76, [6],* 1972, 940-943

[51]   G.Socrates, Inorganic Compounds and Coordination Complexes, in *Infrared and Raman Characteristic Group Frequencies* JOHN WILEY & SONS, LTD (Formerly of Brunel, UK, 2001).

[52]   G. I. N. Waterhouse, G. A. Bowmaker, J. B. Metson, The thermal decomposition of silver (I, III) oxide: A combined XRD, FT – IR and Raman spectroscopic study, *Phys. Chem. Chem. Phys., 3,* 20013838-3845.

[53]   T. Ishikawa, S. Akagi., The structures in the system SnO-SiO₂, *Phys. Chem. Glasses, 19,* 1978, 5.

[54]   J. C. Giuntini, W. Granier, J. V. Zanchetta, A. Taha., Sol-gel preparation and transport properties of tin oxide, *J. Mater. Sci. Lett., 9,* 1990, 1383-1388

[55]   P.Siciliano, Preparation, characterization and applications of thin films for gas sensors prepared by cheap chemical method, *Sens. Actuators B, 70,* 2000, 153-164

[56]   Ü. Kersen, M. R. Sundberg, The reactive surface sites and the H₂S sensing potential for the SnO₂ produced by a mechanochemical milling, *J. Electrochem. Soc., 150, 6,* 2003, H129-H134

[57]   N. M. A. Hadia, S. V. Ryabtsev, P. V. Seredin, E. P. Domashevskaya., Effect of the temperatures on structural and optical properties of tin oxide (SnO x) powder *Phys. B 405,* 2010, 313-317

[58]   A. Chorfa, N. B. Khir, F. S. Rubio, J. Rubio, Silver diffusion and coloration of soda lime and borosilicate glasses Part 1: Effect on the transmission and coloration of stained glasses, *Ceram. – Silik., 56 (1),* 2012, 69-75.

[59]   D. D. Jr. Evanoff, G. Chumanov, Synthesis and optical properties of silver nanoparticles and arrays, *Chem. Phys. Chem., 6,* 2005, 1221-1231.

[60]   E. Mari, T. Palacios, Ruby red surface layers on soda-lime silicate glasses obtained by vapor phase ion-exchange, Proceeding of Int. Congress on glass, 1995, 4, 122.

[61]   E. Trave, E. Cattaruzza, F. Gonella, F. Calvelli, A. Quaranta, A. Rahman., G. Mariotto, Ag clustering investigation inlaser irradiated glasses by optical and vibrational spectroscopy, *Appl. Surf. Sci., 258,* 2012, 9399-9403.

[62]   Q. Zhang, Z. Chen, L. ZhiXin, Simulation of tin penetration process in the surface layer of soda-lime-silica float glass, *Sci. China Tech. Sci., 54, 3,* 2011, 691-697, doi: 10.1007/s11431-010-4259-y

[63]   Y. Hayashi, K. Matsumoto, M. Kudo, The diffusion mechanism of tin into glass governed by redox reactions during the float process, *J. Non-Cryst. Solids, 282,* 2001, 188-196.

[64]   S. I. Sil`vestrovich, E. M. Akimova, M. Z. Mirkina, Thermochemical modification of the structure, physical and mechanical properties of glass, *Fiz.Khim.Stekla, 11[2],* 168-173 1985 (in Russ.).

[65]   O. A. Gladushko., A. G. Chesnokov., Identification of Float Glass Surfaces, *Glass Ceram., 62, 9,* 2005, 308-309

[66]   M. Yamane, S. Shibata, A. Yasumori, T. Yano, H. Takada, Structural evolution during Ag⁺/Na⁺ ion exchange in a sodium silicate glass, *J. Non-cryst. Solids, 203,* 1996, 268-273

[67]   Akimova E.M., Barinova, Diffusion coloration of industrial thermally polished lass with solid- phase copper-containing reagents, *Glass Ceram., 65,* 9-10, 2008.