

# Nanostructured Float-Glasses after Ion-exchange in Melts Containing Silver or Copper Ions

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**Abstract** Ion-exchange technique is widely used for obtaining coloured glasses. In this research we treated float glass samples in vapour and melts of copper and silver containing mixtures. We have studied the influence of experimental conditions (composition of the melt, temperature and processing time, additional treatment) on the size of colloidal nanoparticles, the optical characteristics and the achieving a variety of colour shades of the ion-exchange glasses. We have clarified the role and influence of the presence of tin ions in the surface layer of the glass matrix on the transmission of the glasses, the mechanism for the formation of the colour layer, the depth penetration and the size of colloidal nanoparticles. The optical properties of the nanostructured glasses were investigated by UV-VIS spectrophotometer. The structural and microstructural properties in the glass matrix, showing the formation of nanocrystalline particles have been studied using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) and Scanning electron microscopy (SEM). The particle size and the roughness of the background of the structure have been determined by AFM.

**Keywords** Ion-exchange, Float Glass, Nanoparticles, Copper, Silver

## 1. Introduction

The vitreous state has unique properties related to disordered structure of the glasses and the structural changes accompanying the glass transition. These specifications can be used to obtain new glassy materials by controlling the composition and structure of the glass matrix. Different techniques for modifying the vitreous surface were described in details by Norris and Povey as the most widely is the application of ion-exchange method[1, 2]. Ion-exchange processes between melt and glass surface were performed highly intensively during the 70s of the last century in connection with the modifying of some properties of the glasses: increasing of mechanical strength, chemical resistance[3-8] photochromic properties[9], optical absorption and colouring[10-13]. One of the important properties of modifying ions is their high mobility in the glass, due to their unique electronic configurations. The mobility of an ion also depends on its place in the lattice, thus the investigation of the preferential place for modifying ions is important to develop new functional glasses not only changing the refractive index, but also making it with photoluminescence properties[14-16]. It has been found that

surface treated glasses are promising candidates for many new applications: optoelectronic components, nonlinear optical materials[17-22] and planar waveguides[23-29]. Therefore it is a topical search to study new ways to modify the glass surface controlling diffusion processes[30-39]. The generation of nanosized metal particles in amorphous matrix, the changes of the optical properties and the intensity of the colouring of the new materials were analyzed based on Surface Plasmon Resonance (SPR) [40-47]. Formation of copper and silver nanoparticles, shape, size and their distribution in the glass matrix and the structural changes in the glass after ion - exchange are established using classical and modern analysis techniques such as optical microscopy, UV-VIS spectrometry, TEM, HRTEM, XRD, EXAFS, XPS. In our previous research connected with the application of ion-exchange process for staining of industry glasses we developed a method for obtaining coloured glass type "copper ruby" after treatment in melts containing Cu ions and subsequent UV and X-ray irradiation at appropriate thermal treatment[48]. We also investigated the colouring of glasses treated in silver-containing molten salt. The study of the spectral characteristics of ion exchange coloured glasses shows an absorption peak at 430-450 nm (colouring with silver ions) and 550-650 nm (with copper ions). It is proved that its appearance is a result of the formation of colloidal Ag or Cu particles[49]. Investigations by other authors[50-58] prove the relation between the change in the spectra kinds and the

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intensity of the absorption peak of the content of Ag or Cu which diffuse into the surface layer of the glass and the size of colloidal particles. It was found that the deep profile of the generated particles is strongly influenced by the concentration of modifying ions in the surface layer of the glass, the gas environment in which ion exchange is carried out and the composition of the glass. Growing interest in the study of ion-exchange processes and their applications in various fields, as well as our previous experience on the colouring of the industry glass motivates us to continue our research in this direction. As an object in this research we have to study the peculiarities of ion-exchange processes for treatment of float-glass in melts containing silver or copper ions, to clarify the role and influence of the tin ions contained in the composition of the glass matrix on these processes, the formation of nanoparticles in the surface layer of the ion-exchange glasses and the influence of the ion-exchange conditions on the size and aggregation of colloidal particles, the intensity of colouring and optical characteristics of the glass.

## 2. Experimental

The experiments were conducted on samples of float-glass with composition  $72\text{SiO}_2 \cdot 13\text{Na}_2\text{O} \cdot 8\text{CaO} \cdot 4\text{MgO} \cdot 2\text{Al}_2\text{O}_3$  (wt %) and size  $25 \times 20 \times 3$  mm. They were treated in vapour and melts of several salt mixtures presented in Table 1

The melting of mixtures was carried out in a vertical electrical furnace. The glass samples were immersed in molten bath in porcelain crucible and processed to ion-exchange under the following conditions: for silver containing

molten salt the temperature and time are respectively  $400^\circ\text{C}$ , 5-45 min; for copper sulphate melts –  $550$ - $610^\circ\text{C}$ , 5-30 min and for copper chloride vapour and melts  $500$ - $550^\circ\text{C}$ , 10-60 min. After the ion-exchange, the samples are immersed in diluted solution of HCl and washed in  $\text{H}_2\text{O}$ . The ion-exchanged samples are subject to additional thermal treatment at  $600^\circ\text{C}$ , 1-3h.

UV-VIS spectra were recorded on UV-VISIBLE (Cary 100-Varian) spectrophotometer in the 300-800nm range. 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) and Scanning electron microscopy (SEM-JEOL 5510). Particle size and roughness of the structure are registered by AFM (Nano Scope Tapping Mode TM). The ion-exchange conditions are given in Table 2

## 3. Results and Discussion

The results of the ion-exchange indicate that glasses treated in binary sulphate melts are coloured in red, red-brown and red with the presence of greenish spots which rise with the increase of the concentration of Cu ions in the melt. The glass surface is smooth. Insignificant corrosion occurs in samples treated at higher temperatures and longer processing time. Samples treated in ternary copper sulphate melts are coloured in yellow-green and blue-green. The surface is corroded and the corrosion rises with the increase of time of the ion-exchange process.

**Table 1.** Chemical compositions of salt baths

Composition	$\text{CuCl}$ , mol%	$\text{KCl}$ , mol%	$\text{CuSO}_4$ , mol%	$\text{ZnSO}_4$ , mol%	$\text{Na}_2\text{SO}_4$ , mol%	$\text{K}_2\text{SO}_4$ , mol%	$\text{AgNO}_3$ , mol%	$\text{NaNO}_3$ , mol%	Colour
1	80	20	---	---	---	---	---	---	pink reddish
2	---	---	35	---	65	---	---	---	Red
3	---	---	45	---	55	---	---	---	Red brown
4	---	---	50	30	20	---	---	---	yellow brown
5	---	---	50	20	30	---	---	---	yellow green
6	---	---	50	10	40	---	---	---	yellow green
7	---	---	50	30	---	20	---	---	blue green
8	---	---	50	20	---	30	---	---	yellow green
9	---	---	50	10	---	40	---	---	yellow green
10	---	---	---	---	---	---	1	99	Brown
11	---	---	---	---	---	---	5	95	Brown
Composition	$\text{CuCl}$ , mol%	$\text{KCl}$ , mol%	$\text{CuSO}_4$ , mol%	$\text{ZnSO}_4$ , mol%	$\text{Na}_2\text{SO}_4$ , mol%	$\text{K}_2\text{SO}_4$ , mol%	$\text{AgNO}_3$ , mol%	$\text{NaNO}_3$ , mol%	Colour
1	80	20	---	---	---	---	---	---	pink reddish
2	---	---	35	---	65	---	---	---	Red
3	---	---	45	---	55	---	---	---	Red brown
4	---	---	50	30	20	---	---	---	yellow brown
5	---	---	50	20	30	---	---	---	yellow green
6	---	---	50	10	40	---	---	---	yellow green
7	---	---	50	30	---	20	---	---	blue green
8	---	---	50	20	---	30	---	---	yellow green
9	---	---	50	10	---	40	---	---	yellow green
10	---	---	---	---	---	---	1	99	Brown
11	---	---	---	---	---	---	5	95	Brown

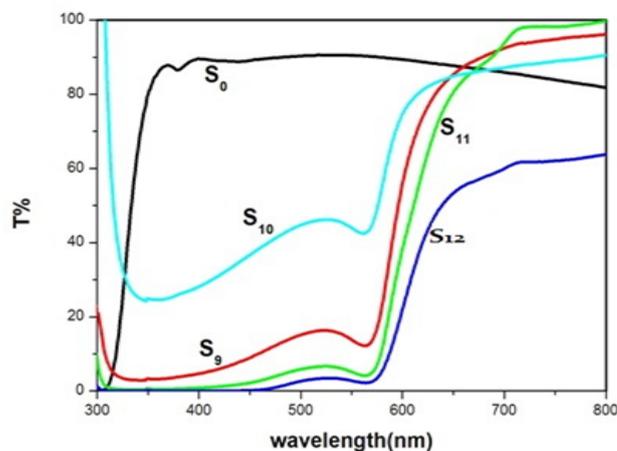
**Table 2.** Ion-exchange conditions of treated samples

Sample	Composition	Ion-exchange T(°C)-τ (min)		Additional treatment T(°C) τ (h)	
S0	-----	-----	-----	-----	-----
S1	1(vapor)	500	30	-----	-----
S2	1(vapor)	500	30	600	1
S3	1(vapor)	500	60	-----	-----
S4	1(vapor)	550	30	-----	-----
S5	1(vapor)	500	10	-----	-----
S6	1(vapor)	500	10	-----	-----
S7	1(melt)	500	10	-----	-----
S8	2(melt)	550	10	-----	-----
S9	2(melt)	550	10	-----	-----
S10	2(melt)	550	10	600	3
S11	2(melt)	550	15	-----	-----
S12	2(melt)	600	10	-----	-----
S13	3(melt)	550	10	-----	-----
S14	3(melt)	600	15	-----	-----
S15	4(melt)	600	15	-----	-----
S16	5(melt)	600	15	-----	-----
S17	7(melt)	600	5	-----	-----
S18	7(melt)	600	10	-----	-----
S19	7(melt)	600	15	-----	-----
S20	7(melt)	550	5	-----	-----
S21	8(melt)	600	15	-----	-----
S22	9(melt)	600	15	-----	-----
S23	10(melt)	400	10	-----	-----
S24	11(melt)	400	10	-----	-----
S25	11(melt)	400	45	-----	-----

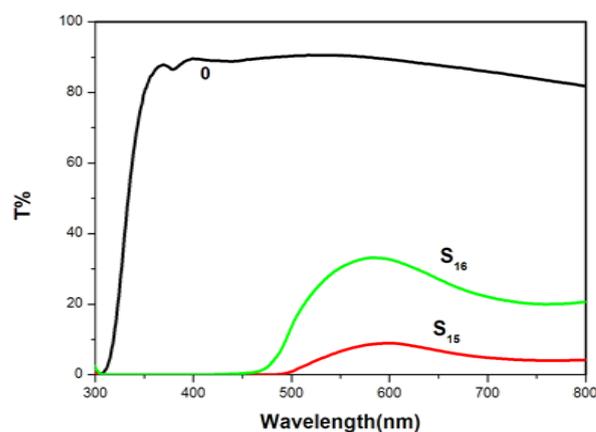
It is found that whatever the treatment, all samples have a smooth, evenly coloured brown surface for the glasses treated in silver nitrate melt. Significant difference is not observed in the intensity of the colouring in longer treatment. Samples treated in vapour or melts of copper chloride salt are coloured in pink reddish. It is worth noting that the surface remains smooth, with no visible corrosion and it is evenly coloured.

In Figure 1 are shown UV-VIS spectra of the samples treated in copper sulphate melt with composition 35CuSO<sub>4</sub>:65Na<sub>2</sub>SO<sub>4</sub>, mol%. The transmission of the glasses decreases with increasing time and temperature of ion exchange treatment compared with the untreated sample S<sub>0</sub>. The cut-off wavelength of the transmission shifts from 300 to 450nm. The additional treatment leads to increasing of the transmission. The registered absorption peak around 560-650 nm is related with formation of colloidal size copper particles.

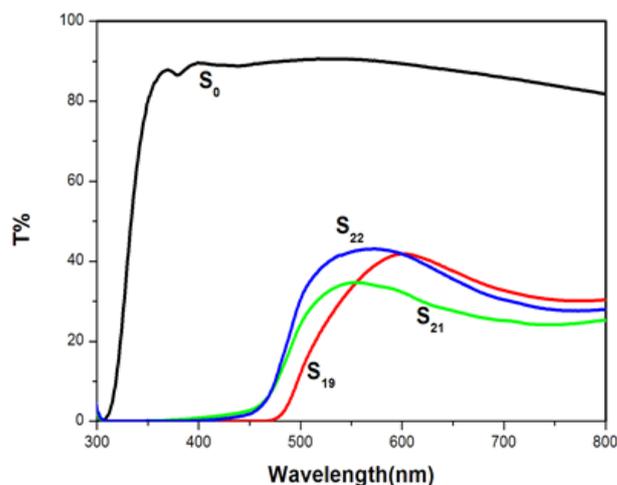
Replacement of Na<sub>2</sub>SO<sub>4</sub> with ZnSO<sub>4</sub> in quantities of 10-30mol% under the same conditions of ion exchange leads to a significant change in the type of UV-VIS curves (Fig. 2).



**Figure 1.** Transmission spectra of float glasses treated in the melt of a sulphate mixture containing 35mol%CuSO<sub>4</sub>, 65mol% Na<sub>2</sub>SO<sub>4</sub> at dependence of temperature, processing time and additional treatment



**Figure 2.** Transmission spectra of float glasses ion-exchange treated at 600°C for 15min in ternary melts with compositions: S<sub>15</sub>-50mol% CuSO<sub>4</sub>, 30 mol% ZnSO<sub>4</sub>, 20mol%Na<sub>2</sub>SO<sub>4</sub>; S<sub>16</sub>-50mol% CuSO<sub>4</sub>, 20 mol% ZnSO<sub>4</sub>,30mol%Na<sub>2</sub>SO<sub>4</sub>

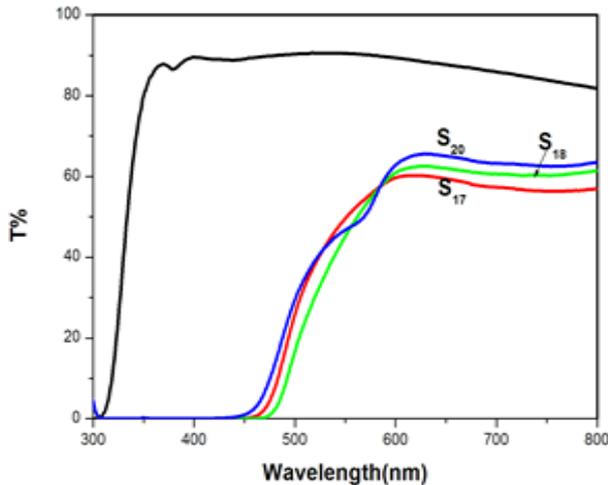


**Figure 3.** Transmission spectra of float glasses ion-exchange treated at 600°C, 15min in ternary melts with compositions; S<sub>19</sub>- 50mol% CuSO<sub>4</sub>, 30 mol% ZnSO<sub>4</sub>, 20mol% K<sub>2</sub>SO<sub>4</sub>, S<sub>21</sub>- 50mol%CuSO<sub>4</sub>,20 mol% ZnSO<sub>4</sub>, 30mol% K<sub>2</sub>SO<sub>4</sub>; S<sub>22</sub>- 50mol% CuSO<sub>4</sub>, 10mol% ZnSO<sub>4</sub>,40mol% K<sub>2</sub>SO<sub>4</sub>

The transmission sharply decreases, the cut-off wavelength of the transmission shifts to 500nm, an absorption peak was not observed, which suggests the absence of Cu colloidal particles in ion exchange layer of glass. This result is in good agreement with the observed visual change in the colour of the glass, from reddish brown to yellow-green (see Table 1)

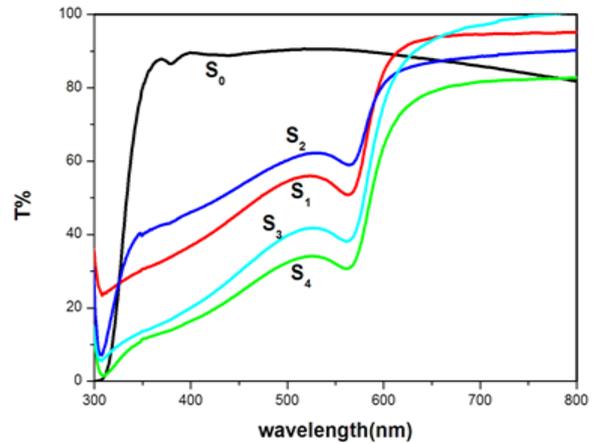
The complete replacement of Na<sub>2</sub>SO<sub>4</sub> with K<sub>2</sub>SO<sub>4</sub> in the composition of the salt bath does not lead to a significant shift of the cut-off wavelength of the transmission. In this case an absorption peak on the spectrum, proving the formation of colloidal copper particles is absent (Figure 3).

At permanent composition of the salt bath and ranging temperature and processing time, the curves of transmission have similar character, slight displacement of the cut-off wavelength of transmission from 440 to 470nm and the absence of an absorption peak around 560nm was observed (Fig. 4).

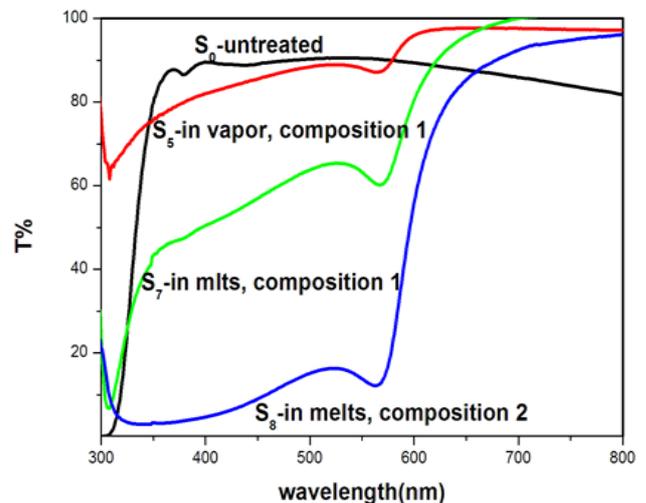


**Figure 4.** Transmission spectra of float glasses treated in the ternary melts with composition- 50mol%CuSO<sub>4</sub>, 30mol% ZnSO<sub>4</sub>, 20mol%K<sub>2</sub>SO<sub>4</sub>, depending on temperature and processing time; S<sub>17</sub>-600°C, 5min; S<sub>18</sub>-600°C, 10min; S<sub>20</sub> – 550°C, 5min

If colouring copper ions in the composition of the melt are introduced in the form of CuCl and the treatment of the glasses is carried out in vapour or melts, the colour of the glass will be pink reddish, different from that of the samples treated in copper sulphate melt. The spectra of glasses after ion exchange in vapour (Figure 5) compared with the spectra of the untreated glass indicate that with the increase of temperature and time of ion exchange the transmission in the visible range decreases. The transmission increases again above 600 nm (in the near infrared range). An absorption peak is registered in the 560-570 nm region due to the formation of colloidal copper particles[59] The additional heat treatment after ion exchange leads to the increase of the transmission of the glasses. This could be explained by the displacement of the equilibrium  $\text{Cu}^+ \leftrightarrow \text{Cu}^0$  to the left[11, 49].



**Figure 5.** Transmission spectra of float glasses treated in vapour of a chloride melt containing 80 mol% CuCl, 20mol% KCl: S<sub>0</sub>- an untreated glass sample; S<sub>1</sub> - an ion-exchanged sample treated at 500°C for 30min without additional treatment; S<sub>2</sub>- an ion-exchanged sample additionally heat treated at 600°C for 1h; S<sub>3</sub> - an ion-exchanged sample treated at 500°C for 60min without additional treatment; S<sub>4</sub>-an ion-exchanged sample treated at 550°C for 30min without additional treatment



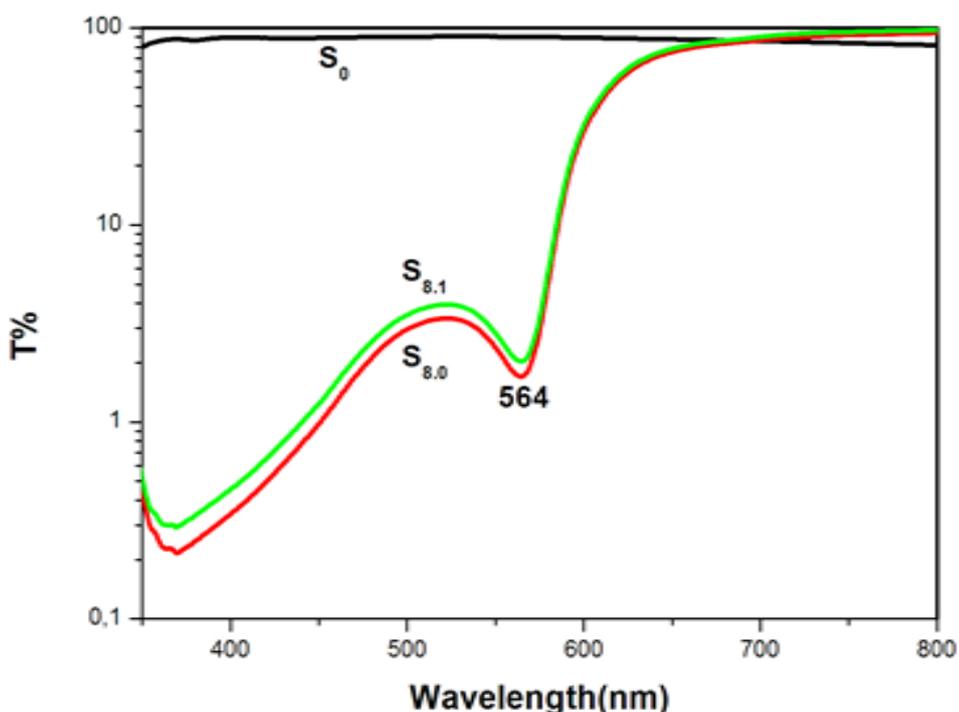
**Figure 6.** Transmission spectra of float glasses treated in vapour or melts of copper containing salt at permanently ion-exchange time (10 min)

Comparing UV-VIS spectra of glasses treated in vapour and melts of copper chloride containing salt and these of copper sulphate containing melt (Figure 6), it is observed that the glasses treated in vapour have the highest transmission and the lowest – in copper sulphate melt. In all three cases is registered an absorption peak around 565nm with different intensity and area characteristic of red ruby glasses. The change of area and position of this peak is associated with changes in the intensity of colour, particle size, their aggregation and depth penetration of the colouring ions in the surface layer of the glass. According to the reference books[8, 42, 48, 49, 53] the increasing area of the absorption peak and its shift to larger wavelengths is evidence of increasing the size of the colloidal particles and the depth of penetration into the surface layer of the glass.

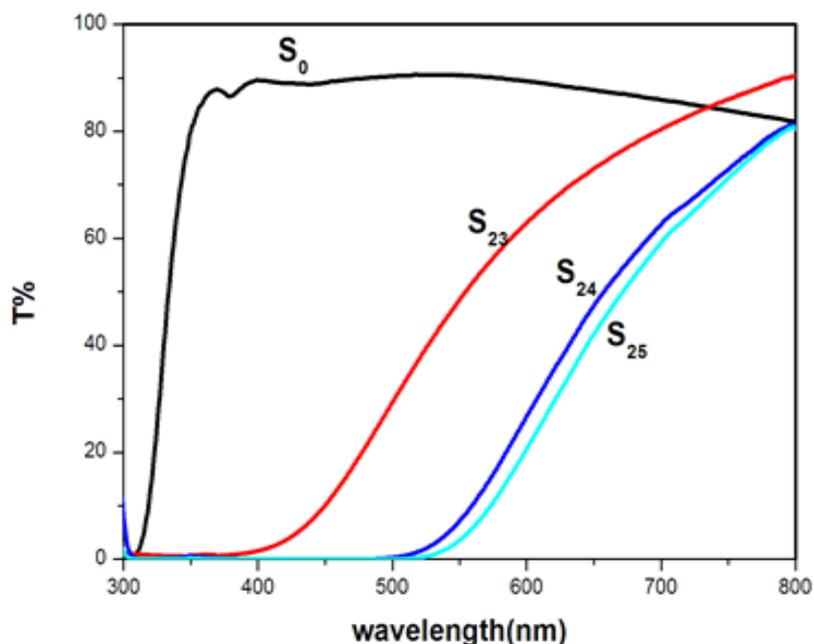
Linking these data with the present studies (Figure 6) show that treatment in the copper sulphate melt allows penetration of colouring ions in the surface layer to a considerable depth, the formation of colloidal particles with the largest size and the most intense red colouring of the glasses. The lowest intensity of colouring was observed after ion exchange in vapour, which can be explained by the small size of the obtained particles and their lower penetration into the surface of the glass.

Additional research related to clarifying the role of tin ions on the ion exchange process was made. For this purpose, the spectra were taken on both surfaces of the float-glass treated in copper-containing melts - top (without Sn ions) and bottom (with Sn ions) (Figure 7).

The spectra show that the transmission of the top side of the sample is higher than that in the presence of Sn ions.

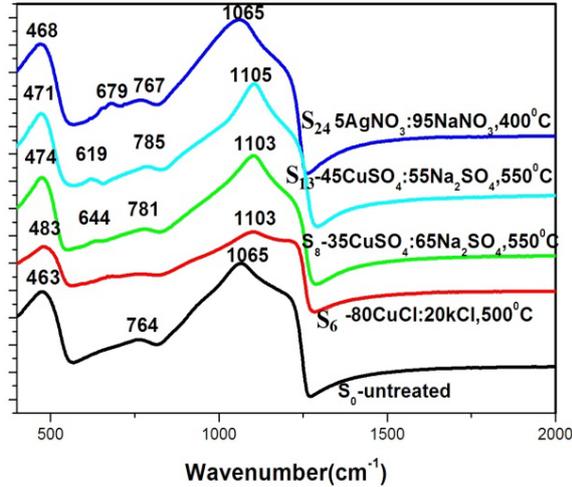


**Figure 7.** Transmission spectra of float glasses treated in copper sulphate containing salt with composition 35mol%CuSO<sub>4</sub>, 65mol%Na<sub>2</sub>SO<sub>4</sub> depending on presence of tin ions in the glass surface; S<sub>8.0</sub>-bottom; S<sub>8.1</sub>-top



**Figure 8.** Transmission spectra of float glasses treated in melts of silver containing salt depending of concentration of AgNO<sub>3</sub> at permanent temperature and different ion-exchange time

At the same time there is a difference in the area of the absorption peak, which confirms the important role of Sn ions in the surface layer on the processes of formation and aggregation of colloidal particles depending on their concentration and oxidation state, as seen in the following papers[60-66]

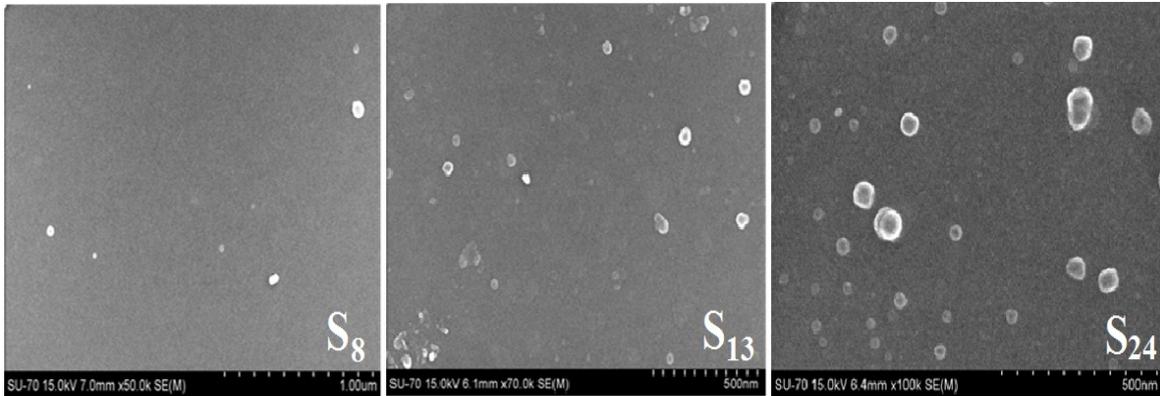


**Figure 9.** DRIFT spectra of float glasses treated in melts with different composition of molten salt at permanently processing time (10 min)

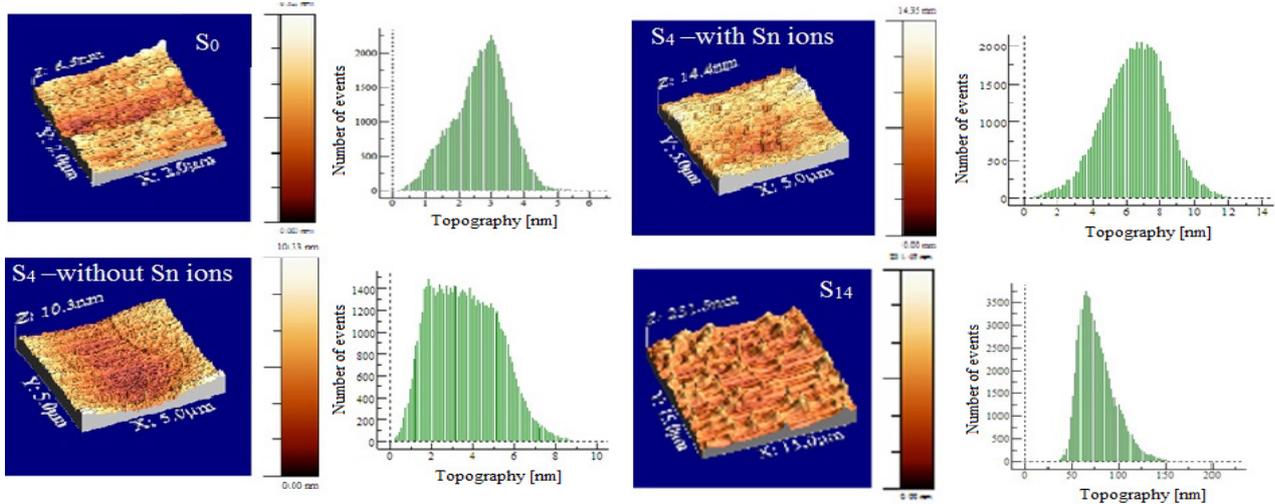
If the samples are treated in silver containing melts visually the intensity of colouring is slightly influenced by the concentration of silver in the melt under changing conditions. UV-VIS spectra (Figure 8) show a decrease in the transmission with increasing ion-exchange time and concentration of Ag ions in the salt bath. The cut-off wavelength of transmission varies from 400 to 520nm.

The structural and microstructural changes occurring in the silicate network after ion exchange were observed by DRIFT spectrometry (Figure 9).

On IR spectra a shift of the main Si-O stretching band from 1065cm<sup>-1</sup> to 1109 cm<sup>-1</sup> and Si-O bending band at 476cm<sup>-1</sup> was observed due to structural transformation. These changes in the reference books associated with depolymerization of the silicate network under the influence of modifying ions[67-71]. Bands characteristic of Cu<sub>2</sub>O and CuO and AgO and Ag<sub>2</sub>O are not observed on the spectra which allows the assumption that copper and silver are present in the form of nanoparticles of elemental copper and silver. Peaks that appear around 400 and 800 cm<sup>-1</sup> are evidence that during ion-exchange treatment the surface layer of the glass crystallization processes occur[63].



**Figure 10.** SEM micrographs of ion-exchange treated glasses for 10 min in melts with different composition: S8-35mol%CuSO<sub>4</sub>, 65mol%Na<sub>2</sub>SO<sub>4</sub>; S13-45mol%CuSO<sub>4</sub>, 55mol%Na<sub>2</sub>SO<sub>4</sub>; S24-5mol%AgNO<sub>3</sub>, 95mol%NaNO<sub>3</sub>



**Figure 11.** AFM images of an untreated glass sample (S<sub>0</sub>) and the samples treated in vapor for 30min (S<sub>4</sub>) or melt for 15min (S<sub>14</sub>) after ion-exchange occurring in copper-containing salt at 550°C

In confirmation the data, SEM analysis can be shown (Fig.10). Presence of nanocrystalline particles with spherical shape and size, ranging from 50 to 100 nm was observed on the micrographs

Three-dimensional AFM images are presented for a better clarification of the topography of nanostructured ion-exchange glasses and determining the surface roughness and the size of formed nanoparticles. The analysis confirms the results of SEM and the roughness of the background surface shows an increase of 3 – 4 nm (for untreated sample) to 6-8nm (for treated in copper chloride melt). The roughness was increased to around 70nm for the sample processed in copper sulphate melt (Figure 11). The size of the formed nanoparticles is ranging from 10-12 to around 150nm, depending on the ion exchange conditions. These results are further evidence of the significant influence of Sn ions contained in the surface layer of float glass on the size of the nanosized particles, their depth penetration and glass colouring.

Summarizing the results of all experimental studies allows to make an overall discussion on the influence of ion exchange conditions for obtaining nanostructured coloured glasses with different shades. The analysis confirms the discussed mechanism in the paper[53] for the formation of the colour layer in the float-glass surface including interdiffusion ( $\text{Na}^+ \leftrightarrow \text{Cu}^+$ ); reduction of  $\text{M}^+$  to  $\text{M}^{0+}$  ( $\text{M} = \text{Cu}, \text{Ag}$ ) was favoured by less oxidation forms of the tin ( $\text{Sn}^0, \text{Sn}^{2+}$ ) are located in the surface layer and finally a growth of colloidal Cu clusters by diffusion that determine the red (brown) colour of ion-exchange glass, evidenced by the appearance of a resonance peak at 560-650nm for copper and 420nm for silver colloidal nanoparticles. Introduction of Zn ions to some rate in the composition of the melt prevents the reduction of the copper ions and the obtained glasses are coloured in yellow green and blue green, depending on the type of the predominant particles. The concentration of  $\text{Zn}^{2+}$  in the salt bath is decisive for the glass colour and the corrosion degree. The lower content of  $\text{ZnSO}_4$  prevents corrosion on the surface only when as a third component in the initial batch  $\text{K}_2\text{SO}_4$  was submitted instead of  $\text{Na}_2\text{SO}_4$ .

Significant decrease of the transmission of ion-exchange samples with increasing of the temperature and ion-exchange time can be explained by the depth penetration in the glass matrix of a significant amount of copper or silver nanoparticles[40, 53, 64]. Moreover the significant decrease in the transmission of the samples can be associated with changes in physical and mechanical properties of the glasses[8]. It is proven that a decrease of the transmission is accompanied with an increase in microhardness and mechanical strength of glass and these changes are bound with the concentration of copper or silver nanoparticles in the surface layers of the glass.

Based on the results of our experimental studies it can be assumed that the samples treated in copper sulphate melt have a high concentration of copper nanoparticles penetrated to a considerable depth in the glass matrix respectively they have better physical and mechanical properties

## 4. Conclusions

Depending on the conditions of the ion exchange process (composition of the melt, temperature and processing time, the kind of colouring ions) coloured glass with different shade (yellow-green and blue-green, red ruby, red brown and brown) can be obtained.

It was found that with increasing the ion exchange time and temperature, the transmission of treated glasses in the visible range significantly decreases and the cut-off wavelength of the transmission shifts from 300 to 520nm.

Red ruby glasses is possible to be obtained only after ion exchange treatment of float glass in vapour or melts of binary copper chloride and copper sulphate molten salt. On the UV-VIS spectra of these glasses an absorption peak in 560-570 nm range is registered, proving the formation of copper colloidal nanoparticles. The appearance of this peak, as well as new characteristic bands on the DRIFT spectra of the studied samples in the range of  $400\text{-}800\text{ cm}^{-1}$  are a strong evidence of the beginning of crystallization processes occurring on the surface of the ion-exchange coloured glasses.

To prevent corrosion of the surface of the glass treated in ternary melts ion exchange treatment is required to be performed at a lower temperature ( $550^\circ\text{C}$ ), less processing time (5-10min), the amount of  $\text{ZnSO}_4$  in the composition of the salt bath should not exceed 10mol% and  $\text{Na}_2\text{SO}_4$  to be replaced with  $\text{K}_2\text{SO}_4$ .

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## REFERENCES

- [1] E Norris, *Making stained glass*, Glass, 57, 219, 1980
- [2] W. R. Povey, *Vitreous enamelling on glass*, Glass, 57, 204-207, 1980
- [3] S.S.Kistler, *Stresses in glass produced by nonuniform exchange of monovalent ions*, J. Amer. Ceram. Soc. 45[2], 59-68, 1962.
- [4] M. E. Nordberg, E. L. Mochel, H. M. Garfinkel, J. S. Olcott, *Strengthening by Ion Exchange*, J. Amer. Ceram. Soc., 47, 5, 1964
- [5] J. B. Ward, B. Sugarman., C. Symmers, *Studies on the Chemical Strengthening of soda-lime-silica glass*, Glass

- Technology, 63, 90, 1965
- [6] E. W. Deeg, *Ion Exchange strengthened silicate glass filter for ultraviolet light*, U. S. Patent, 4, 022, 628, 1977
- [7] A. Bankov, Y. Dimitriev, Y. Ivanova, E. Gatev, L. Ivanova, *Chemical hardening of lens for spectacles*, J.Stroit.Mater.I Silikat.Prom., 3, 19, 1980 (in Bulg.)
- [8] S. I. Sil'vestrovich, E. M. Akimova, M. Z. Mirkina, *Thermochemical modification of the structure and physicochemical properties of glass*, Fiz.Khim.Stekla, 11[2], 168-173 1985 (in Russ.).
- [9] H. Garfinkel, *Photochromic glass by silver ion exchange*, Appl. Optics 7, 5, 1968
- [10] G. H. Frishcat, *Coloring of glass surfaces by ion-exchange*, J Non-Cryst Solids 19, 367-368A, 1975
- [11] Y. Dimitriev, Y. Ivanova, I.Stavrakeva, D.Kashcieva, *Ion exchange processes in multicomponent glassy systems*, Stroit. Mater. I silikat. Prom. 7-8, 39, 1976 (in Bulg.)
- [12] K. Kobayashi, *Optical and EPR studies on redox interaction layers of Ag<sup>+</sup> and Cu<sup>+</sup> ions diffusing into soda-lime glass*, Phys. chem. glasses, 20[2], 21-24, 1979
- [13] 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], 230-234, 1986 (in Russ.)
- [14] D. Manikandan, S. Mohan, K.G.M. Nair, *Photoluminescence of embedded copper nanoclusters in soda-lime glass*, Mater. Lett. 57, 1391-1394, 2003
- [15] Doris Ehr, *Photoluminescence in the UV-VIS region of polyvalent ions in glasses*, J. Non-Cryst. Solids, 348, 22-29, 2004
- [16] Y. Tia, X. Hea, J. Zhanga, J. Zheng, P. Wang, G. Farrell, *Cu-Na Ion Exchange Soda-Lime Glass Planar Waveguides and Their Photoluminescence*, Proc. of SPIE-OSA-IEEE, 7630, 76301C-1, 2009
- [17] Y. Yonesaki, K. Miura, R. Araki, K. Fujita, K. Hirao, *Space-selective precipitation of non-linear optical crystals inside silicate glasses using near-infrared femtosecond laser*, J. Non-Cryst. Solids, 351, 885-892, 2005
- [18] Y. XiuChun, L. ZhiHui, L. WeiJie, X. JingXian, D. Zhiwei, Qian Shixiong, *Optical nonlinearity and ultrafast dynamics of ion exchanged silver nanoparticles embedded in soda-lime silicate glass*, Chinese Science Bulletin, 53[5], 695-699, 2008
- [19] J. Qiu, K. Miura, K. Hirao, *Femtosecond laser-induced microfeatures in glasses and their applications*, J. Non-Cryst. Solids 354, 1100-1111, 2008
- [20] Y.H. Wang, Y.M. Wang, J.D. Lu, L.L. Ji, R.G. Zang, R.W. Wang, *Nonlinear optical properties of Cu nanoclusters by ion implantation in silicate glass*, Optics Communications 283, 486-489, 2010
- [21] [Y. Chen, J. Jaakola, A. Sayn Atjoki, A. Tervonen, S. Honkanen, *SERS-Active Silver Nanoparticles in Ion-Exchanged Glass*, J. Nonlinear Opt. Phys. Mater. 19[4], 527-533, 2010
- [22] G. Lin, D. Tan, F. Luo, D. Chen, Q. Zhao, J. Qiu, *Linear and nonlinear optical properties of glasses doped with Bi nanoparticles*, J. Non-Cryst. Solids 357, 2312-2315, 2011
- [23] P. Nebolova, J. Spirkova, V. Perina, I. Jirka, K. Mach, G. Kuncova, *A study of preparation and properties of copper-containing optical planar waveguides*, J. Solid state ionics 141-142, 609-615, 2001
- [24] R. Rogozinski and P. Karasinski, *Optical waveguides produced in ion exchange process from the solutions*, Opto electronics Review 13[3], 229-238, 2005
- [25] J-M. Lehy, D. Erni, F. Robin, L. Dellmann, R. Dangel, B. J. Offrein and Werner Bächtol, *Low-loss copper film ion-exchanged optical waveguides with step-like index profiles in glass*, Lasers and Electro-Optics Society, 2005., The 18th Annual Meeting of the IEEE, 800-801, 2005
- [26] J.-M. Lekhy, *Optical waveguides with copper film Ion-exchange in glass*, DISS. ETH №16496, 2006
- [27] L. Huang, X. Chen, Y. Yang, Y. Xia, *Fabrication and Characterization of Copper-Exchanged BK7 Waveguides*, J. Korean Phys. Soc., 51[4], 1517-1520, 2007
- [28] Online Available: <http://dx.doi.org/10.1080/014680302753339411>
- [29] H. XIA, C. Teng, X. Zhao, J. Zheng, *Refractive Index Profiles of Copper Ion Exchange Glass Planar Waveguides*, Chin. Phys. Lett. 29,[8], 084215, 2012
- [30] M. Suszynska, L. Krajczyk, R. Capelletti, A. Baraldi, K.J. Berg, *Microstructure and silver nanoparticles in ion-exchanged and deformed soda-lime silicate glasses*, J. Non-Cryst. Solids 315, 114-12, 2003
- [31] J. Sheng, J. Li, J. Yu, *The development of silver nanoclusters in ion-exchanged soda-lime silicate glasses*, International Journal of Hydrogen Energy 32, 2598-2601, 2007
- [32] A. Ruivo, C. Gomes, A. Lima, M. Butelho, R. Melo, A. Belchior, A. Piros de Matos, *Gold nanoparticles in ancient contemporary ruby glass*, J. Cultural Heritage 9, e134-e137, 2008
- [33] A. Puche-Roig, V. P. Martin, S. Murcia -Maskaros, R. I. Puchades, *Float glass colouring by ion exchange*, J. Culture Heritage 9, 129-133, 2008
- [34] R.S.Varma, D. C. Kothar, R. Tewari, *Nano-composite soda lime glass prepared using silver ion-exchange*, J. Non-Cryst. Solids, 355, 1246-1251, 2009.
- [35] F. Goutaland, E. Marin, H. Gagnaire, J.Y. Michalon and A. Boukenter, *Efficient and Controllable Silver Nanoparticles Generation in Ion-exchanged Soda-lime Glasses by Simultaneous Heat Treatment and UV Exposure*, ujm-00377821, version 1-23 Apr 2009
- [36] T.Suetsugu, T.Wakasugi, K.Kadono, *Compositional dependence of silver ion incorporation into borosilicate glasses through staining process for fabrication of graded-index optical elements*, J. Glass Science and Technology, 50[4], 214-216, 2009.
- [37] 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, 2306-2308, 2011
- [38] E. Travea, E. Cattaruzza, F. Gonellaa, P. Calvelli, A. Quarantab, A. Rahmanc, G. Mariottoc, *Ag clustering investigation in laser irradiated ion-exchanged glasses by*

- optical and vibrational spectroscopy*, Appl. Surf. Sci. 258 9399–9403, 2012
- [39] O. Véron, J.-P. Blondeau, D. De Sousa Meneses, C. An-dreazza Vignolle, *Characterization of silver or copper nanoparticles embedded in Soda-lime glass after a staining process*, Surface & Coating Technology xxx (2012) xxx–xxx (in press)
- [40] S. Takeda, K. Yamamoto, K. Matsumoto, *Coloration due to colloidal Ag particles formed in float glass*, J. Non-Cryst. Solids, 265[1-2], 133-142, 2000
- [41] 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*, Nuclear Instruments and Methods in Physics Research B 198, 73-76, 2002
- [42] 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, 86–91, 2003
- [43] S. Thomas, S. K. Nair, E. Muhammad Abdul Jamal, S H Al-Harhi, M. Raama Varma, M. R. Anantharaman, *Size-dependent surface plasmon resonance in silver silica nanocomposites*, Nanotechnology 19[7], 075710, 2008
- [44] P. Colombari, *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, 109-132, 2009.
- [45] S. Peng, J. McMahon, G. Schatz, S.Gray, Y.Sun, *Reversing the size-dependents of surface Plasmon resonances*, PNAS, 107[33], 14530-14534, 2010
- [46] [M.Suszynska, T. Morawska, L. Krajczyk, *Optical properties of small silver particles embedded in soda-lime silica glasses*, Optica Applicata XL, 2, 2010.
- [47] T. Xu, F. Chen, X. Shen, S. Dai, Q. Nie, X. Wang *Observation of surface Plasmon resonance of silver particles and enhanced third-order optical nonlinearities in AgCl doped Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ternary glasses*, Materials Research Bulletin 45, 1501-1505. 2010
- [48] Y. Dimitriev, Y. Ivanova, E. Gatev, *Method for creating a colour image on glass by ion exchange*, Stroit. Mater. i silikat. Prom., 3-4, 39, 1977 (in Bulg.).
- [49] 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.).
- [50] T. Yoko, T. Nishiwaki, K. Kamiya, S. Sakka, *Cooper-alkali ion exchange of alkali aluminosilicate glasses in copper-containing molten salt: I, monovalent copper salt, CuCl*, J. Am. Ceram. Soc., 74[5], 1104-11, 1991
- [51] T. Yoko, T. Nishiwaki, K. Kamiya, S. Sakka, *Cooper-alkali ion exchange of alkali aluminosilicate glasses in copper-containing molten salt: I, divalent copper salts CuCl<sub>2</sub>, CuSO<sub>4</sub>*, J. Am. Ceram. Soc., 74[5], 1112-16, 1991.
- [52] D. I. Lee, Y. K. Lee, H. S. Lee, *Effects of silver and potassium ions on ion exchange in float glass*, J. Mater. Science 27 2908-2913, 1992
- [53] 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, 4, 122. 1995
- [54] M. Villegas, J. M. Navaro, *Optical spectroscopy of a soda-lime glass exchanged with silver*, Phys. Chem. Glasses, 37[6], 248-53, 1996
- [55] P.Wang, *Thermal activation energy of silver in ion exchanged soda-lime glass investigated by X-ray photoelectron spectroscopy*, Materials Chemistry and physics 50, 213 -218, 1997
- [56] 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, 102–112, 1997
- [57] H. Hofmeister, S. Theil, M. Dubiel, E. Schurig, *Sintesis of nanosized silver particles in ion-exchanged glass by electron beam irradiation*, Appl. Phys. Lett. 70, 13, 1694-1696, 1997
- [58] D'Acapito F., Mobilios, Regnard J.R., Cataruza, F.Gonela, P. Mazzodi, *The local atomic order and the valence state of Cu in Cu-implanted soda-lime glasses*, J. Non-Cryst. solids, 232-234, 364-369, 1998
- [59] 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], 409-414, 2012.
- [60] B. Yangt, P. D. Townsend and S. A. Holgate, *Cathodoluminescence and depth profiles of tin in float glass*, J. Phys. D Appl. Phys. 27, 1757-1762, 1994
- [61] Y. Hayashi, K. Matsumoto, *Mechanisms and chemical effects of surface tin enrichment on float glass*, Glass Technol. 42[4/5], 130-3, 2001
- [62] E. C. Ziemath, B. Z. Saggiaro, J. S. Fossa, *Physical properties of silicate glasses doped with SnO<sub>2</sub>*, J. Non-Cryst. Solids, 351, 3870–3878, 2005
- [63] B. Z. Saggiaro, E. C. Ziemath, *Changes of physical properties of glass surfaces exposed to KNO<sub>3</sub> vapors*, J. Non-Cryst. Solids, 352, 2783–2790, 2006
- [64] E. M. Akimova, O.P. Barinova, *Diffusion coloration of industrial thermally polished glass with solid-phase copper-containing reagents*, Glass and Ceramics 65, 9-10, 2008.
- [65] Q. Zhang, Z. Chen, Z. Li, *Simulation of tin penetration process in the float glass (float glass tin penetration)*, 31[6–7], 1272–1278, 2011
- [66] Y. Yamamoto, K. Yamamoto, *Precise XPS depth profile of soda-lime-silica float glass using C60 ion beam*, Optical materials 33, 1927-1930, 2011
- [67] T. Sequinel, S. Cavab, 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 SnO<sub>2</sub> nanopowders on float glass*, J. Ceramics International 37, 1533–1536, 2011
- [68] J. A. Kapoutsis, E. I Kamitsos, G. D. Chys-sikos, *A structural Study, of Silver Borate Glasses by Infrared Reflectance and Raman Spectroscopy*, Proc. Second Int. Conf. on Borates Glasses, Crystals and Melts, 1996

- [69] P. Colomban, M.-P. Etcheverry, M. Asquier, M. Bounichou, Aure' lie Tournie', *Raman identification of ancient their degree of deterioration*, J. Raman Spectrosc., (www.interscience.wiley.com). DOI: 10.1002/jrs.149
- [70] M. Suszynska, M. Maczka, E. Bukowska and K. J. Berg, *Structure and IRR spectra of copper-exchanged soda-lime silica glass*, Journal of Physics: Conference Series 249, 012048, 2010
- [71] L. H. Abuhassan, N. George, *Syntesys of bright photostable red luminescent Cu nanoparticles*, International Journal of Nanomanufacturing, 7[1], 1-12, 2011