Ag/Na ion exchange in soda-lime glasses and the formation of small Ag nanoparticles

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Abstract

We investigated the formation of very small Ag nanoparticles of 1–2 nm size in soda-lime glass with enhanced amounts of iron oxide by Ag/Na ion exchange procedures. The duration of ion exchange has been chosen between 20 and 600 h to study the processes systematically. It could be shown that structural relaxations take place as the Ag^+ ions were incorporated into the glass replacing the Na^+ of the original matrix. X-ray absorption spectroscopy at the Fe K-edge demonstrated that polyvalent Fe ions served as thermosensitive reductive during the ion exchange well below the glass transformation temperature. The transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) experiments revealed the formation of Ag nanoparticles of sizes from 1.4 to 1.8 nm in surface-near regions for exchange periods up to 400 h at 330 °C. By combination of TEM and EXAFS also the presence of metastable particles like, e.g., argentous species in the process of precipitation of very small particles has been indicated. These silver containing precipitates were transformed into crystalline silver nanoparticles for a prolonged ion exchange duration of ≈600 h.
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1. Introduction

Silver–sodium ion exchange is used frequently for incorporation of silver in glass to obtain composite materials with specific linear and nonlinear optical properties [1,2]. For example, such metal particles can be used to prepare photonic glasses by specific precipitation processes [3]. Considering the ion exchange process, the ionic silver, more or less affected by internal reductives, can be precipitated as nanoparticles in a diffusion-mediated process having a depth-dependent behaviour. From very recent studies on silver nanoparticles-based planar waveguides it is known that particle sizes of only a few nanometres together with appropriate refractive index variations can already be achieved by low-temperature ion exchange without additional thermal processing [4]. However, this requires a certain tuning of the ion exchange parameters as well as selection of suitable composition of the glass and sample geometry. Furthermore,

a combination of methods for chemical and structural characterization is needed to explicate some of the peculiarities of the complex phenomenon and to find out the corresponding correlations to macroscopic properties.

Here, soda-lime glasses with enhanced amounts of polyvalent iron ions as reducing agents were used as base materials. That should enable preparing nanoparticles with a reduced mean particle size in the glass matrix as well as a narrow size distribution. The duration of ion exchange has been varied in the range of 20–600 h to allow a systematic investigation. For other glasses, the particle formation usually requires both the ion exchange and subsequent thermal treatments at elevated temperatures. In this case, the various processes like diffusion of silver ions into the matrix, their reduction, the nucleation and the crystal growth take place under the influence of large gradients of concentrations of different species across the sample.

We have chosen X-ray absorption spectroscopy to study the Ag^+ environment and structural relaxations in the glass matrix in the course of ion exchange as well as to monitor the Fe^{2+}-based internal redox process and the correlation of Ag species to each other from the respective K-edge characteristics.

Energy-dispersive X-ray spectroscopy (EDXS) has been employed for recording silver concentration profiles to investigate the incorporation in the glass. Transmission electron microscopy (TEM) was used to study the formation of Ag nanoparticles and to evaluate the corresponding particle sizes and size distributions. While TEM yields such data on purely local base, enabling to follow the variation with penetration depth, small angle X-ray scattering (SAXS) has alternatively been used to record particles sizes and size distributions by integral measurements. This combination of rather demanding methods enabled clearly to demonstrate the presence of argentous species in the early stage of silver particle formation.

2. Experimental

For silver incorporation and Ag nanoparticle formation we prepared slices (15 mm × 15 mm in square) of commercial soda-lime float glass containing (in wt%) 71.86% SiO_2, 13.30% Na_2O, 8.69% CaO, 4.15% MgO, 0.59% Al_2O_3, 0.31% K_2O, 0.01% BaO, 0.08% TiO_2, 0.15% SO_3 and 0.865% Fe_2O_3. For all samples, the float glass surface that contains tin ions owing to the glass fabrication process has been removed by the grinding procedure before Ag doping by ion exchange. All samples were finished to a thickness of ≈150 μm before the exchange procedure. The silver ions were introduced into the glass network by an isothermal ion exchange with 0.05 wt% $AgNO_3$ in a $NaNO_3$ melt at 330 °C for different durations up to 600 h.

Time and depth dependence of the ion exchange was monitored by EDXS (ESEM E3 at 15 kV) at cross-section bulk samples. For TEM and high-resolution electron microscopy (HREM) examination of the particle formation using JEM 1010 at 100 kV and JEM 4010 at 400 kV, respectively, cross-section specimens were prepared by sawing, mechanical grinding and polishing, as well as ion-beam etching using specimen cooling. Finally, a thin carbon coating was applied to prevent charging effects from the electron beam. Quantitative chemical analysis requires the evaluation of full energy spectra at a certain depth, whereas line profiles in cross-section with element specific energy windows normally provide only qualitative information about the diffusion profiles. Accordingly, always 3 full energy spectra, near both surfaces and in the glass interior, have been recorded to evaluate the background intensities of silver from line intensities recorded at the Rh Kα position, and to calculate correction terms for EDXS line profiles depending on the incorporation of silver. To enhance the precision of the measurements, the EDXS intensities of the silver line profiles additionally were calibrated by atom absorption spectroscopy.

The EXAFS spectra at the Ag K-edge (25.514 keV) and Fe K-edge (7.112 keV) and the near edge range of these spectra were measured at beamline X1 and E4 of HASYLAB (Hamburg, Germany) in transmission mode, utilizing Si(3 1 1) and Si(1 1 1) double-crystal monochromator, respectively. The energy resolution of the experiments was $\Delta E/E \cong 2.5 \times 10^{-4}$. While the Fe K-edge XANES spectra of the glass samples have been measured at liquid nitrogen or RT, the Ag K-edge EXAFS spectra of Ag foil and Ag-containing glass were systematically measured in the temperature range from 10 to 300 K using a liquid helium vapour flow cryostat equipped with an electric heater. The temperature was monitored by a thermocouple mounted on the sample holder. In addition to the spectra measured at the various glass samples, X-ray absorption spectra of bulk metal foils of Ag and Fe as well as of crystalline iron oxides (for example Fe_2O_3) were measured for reference purposes.

Small angle X-ray scattering (SAXS) has been performed at BESSY (Berlin/Germany). A two-dimensional gas detector with delay line readout was used to measure the SAXS intensity at 0.1333 nm. Two sample-detector distances were measured to cover the interesting q range from 0.1 to 7 nm.

3. Results and discussion

3.1. Ag/Na ion exchange analysed by EDXS

The thin plate specimen geometry and low thickness allow a quasi one-dimensional description of the Ag^+/Na^+ interdiffusion assuming a reaction–diffusion system with constant diffusion coefficients. After approximately 10 h delay the surface-near region of the glass exhibits a colouration due to the surface plasmon resonance of Ag nanoparticles. With increasing processing time the particle region spreads deeper into the glass such that after ≈500 h the entire sample becomes coloured. This is demonstrated by the cross-section views shown in Fig. 1 which enable to monitor the progress of colouration due to Ag particles during the ion exchange from a surface-near region to the interior. The sharp transition between coloured and uncoloured region can be described as reaction front (RF).

In contrast to the slower progress of Ag nanoparticle formation into the glass interior, EDXS showed that already upon about 100 h duration of ion exchange Ag species can be found in the centre. Numerical fitting of silver diffusion profiles assuming a drain-free diffusion and constant interdiffusion coefficient yields a certain decrease of this coefficient with processing time (see Fig. 2 and Table 1). That can be
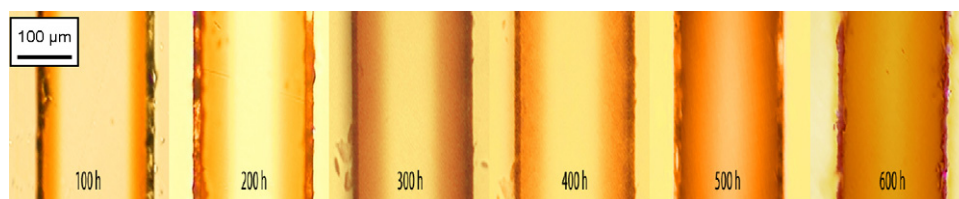

Fig. 1. Cross-section micrographs of the ion-exchanged glass at various stages of processing (thickness always 150 μm).
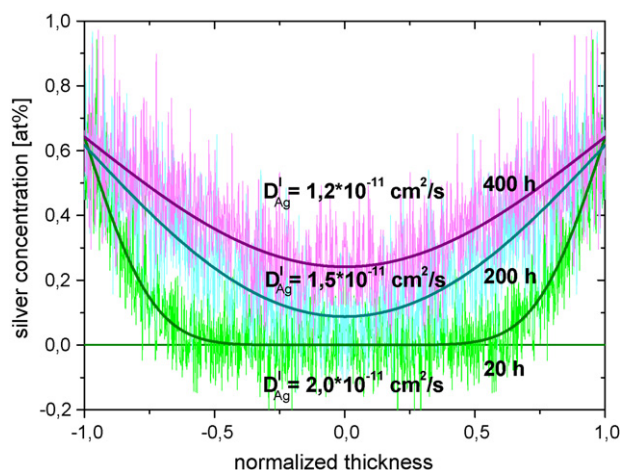
Fig. 2. Calibrated silver concentration profiles for 20, 200 and 400 h ion exchange with the diffusion coefficients marked.
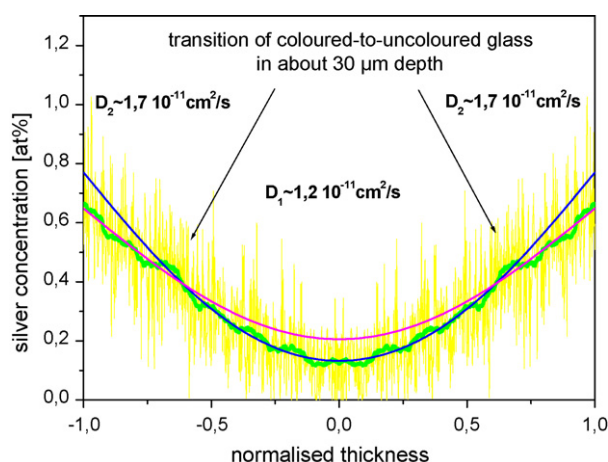

Fig. 3. Silver concentration profile for 200 h ion exchange taking into account a background intensity change which indicates a jump in the diffusion behaviour at the coloured-to-uncoloured transition.

explained by a decrease in the ion exchange rate caused by a finite Ag^+ source. The sodium interdiffusion profiles based on the nominal sodium concentration before processing yield diffusion coefficients being systematically lower than those of silver. A more detailed analysis of the silver diffusion profiles taking into account a changed background intensity caused by the ion exchange procedure reveals that in comparison to the uncoloured interior of the glass the Ag^+ interdiffusion coefficient is enhanced by about 40% in the particles containing layer. This is shown in Fig. 3 for the concentration profile determined upon 200 h ion exchange where the position of change in about 30 μm depth is marked by arrows. This position corresponds

to the position of the reaction front. The silver concentration depth profiles as well as background depth profiles indicate a distinct change of structural as well as diffusive properties caused by the silver incorporation and/or the colouration (see Table 1).

Obviously, this change mainly is caused by some peculiarities of the ion exchange procedure. It was already shown that the incorporation of silver leads to a decrease of the glass transformation temperature for this glass system [5] as well as for other silicate glasses [6] together with a decrease of the thermal expansion coefficient. Moreover, this effect is accompanied by a structural evolution in the silicate structures too [7]. It was suggested that the formation of a twofold oxygen coordination of Ag ions is responsible for all these effects. Therefore, the local environment of silver ions in our samples should be investigated.

3.2. Structural relaxation around Ag ions

The local order around silver ions in the glass and thus the structural modifications due to the Ag/Na ion exchange can be sensitively investigated by EXAFS spectroscopy at the Ag K-edge. The results obtained for the present samples should be discussed in terms of EXAFS parameters like the atomic distances, R, the coordinations numbers, N, and the corresponding Debye–Waller factors, DWF. The latter parameter describes the structural order within the coordination shell of the considered atom. The data presented in Table 2 demonstrate that after silver–sodium ion exchange the value of the Ag–O coordination number is approximately two which is equal to that of crystalline Ag_2O. The Ag–O distance is 2.15 Å. A similar behaviour was already observed for sodium tetrasilicate and sodium aluminosilicate glasses [8], borate glasses [9] and soda-lime glasses with lower amounts of iron [10] as used here. These results show distinct differences compared to the sodium environment of the base glass before the ion exchange. Usually, the Na–O distances in such sodium silicate glasses are 2.3–2.4 Å and the coordination number amounts to approximately five (see for example [8,10]). That means, in spite of the low process temperatures, well below the glass transformation, the silver incorporation causes local rearrangements. Consequently, the

Table 2

EXAFS parameters of the Ag–O coordination of ion-exchanged glasses in comparison with that of crystalline Ag_2O

Sample/exchange duration	$R_{Ag–O}$ (Å)	$N_{Ag–O}$	$DWF_{Ag–O}$ (Å^2)
Glass (150 h)	2.151	1.45	0.0064
Glass (200 h)	2.154	1.44	0.0068
Ag_2O	2.050	2	0.0038

Table 1

Ion exchange rate and interdiffusion coefficients as determined from EDXS concentration profiles; X: Ag–Na exchange rate; D_i: Ag/Na interdiffusion coefficient, calculated from i = Ag, Na

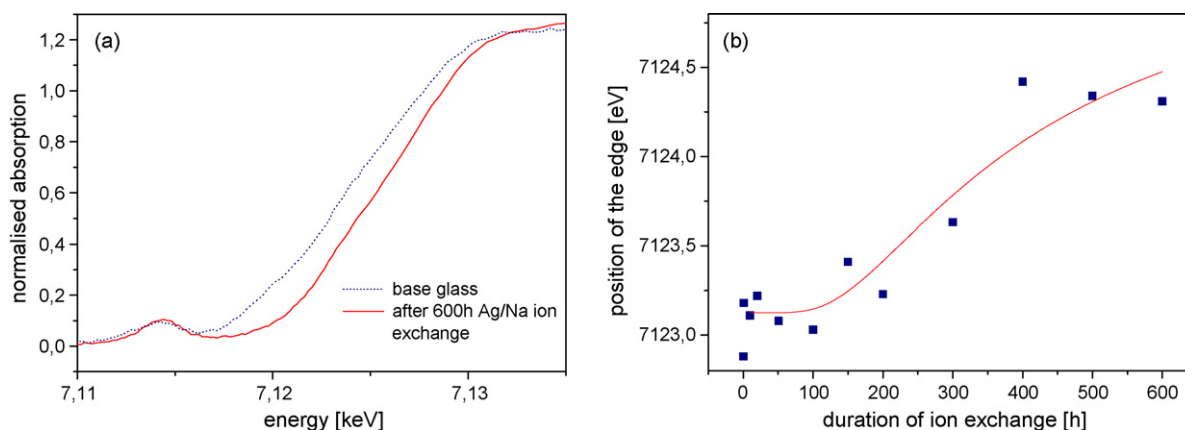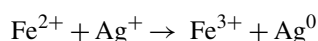| Exchange duration (h)	X (%)	D_{Na} (10^{-11} cm^2/s)	D_{Ag} (10^{-11} cm^2/s)	D_{Ag} (uncoloured) (10^{-11} cm^2/s)	D_{Ag} (coloured) (10^{-11} cm^2/s)
20	11.3	1.8	2.0	–	–
200	8.7	1.2	1.5	1.2	1.7
400	8.7	0.8	1.2	1.0	1.9

Fig. 4. (a) Normalised Fe K-edge XANES spectra of the base glass and after 600 h ion exchange. (b) Shift of the position of the Fe K-edge as a function of the exchange duration.

soda-lime glasses with enhanced amounts of iron oxide show an analogous behaviour with respect to the Ag incorporation as those glasses with less amounts of iron. Some authors [11] explain such structural changes by the enhanced covalent degree of the Ag–O bonding. Thus, in many sodium silicate glasses the formation of silver-like sites in addition or instead of the sodium-like site appears to be caused by the silver–sodium ion exchange. This relaxation can have considerable consequences with respect to the diffusion behaviour as discussed above and with respect to other properties of silver containing glasses. However, this relaxation process takes place around all silver ions embedded into the glass matrix, i.e., upon 200 h exchange it appears within the whole sample (see Fig. 2) and not only in the region up to the reaction front. Therefore, the increase of D'_{Ag} in the coloured region cannot be explained by this effect. That means, the formation of the Ag nanoparticles and the related reduction of silver ions should even more influence the diffusion coefficients.

3.3. Redox reaction with iron ions

The next step of the experiments was to analyse the redox process. Because of the high concentration of polyvalent iron ions in the glasses investigated here, the Fe^{2+} should act as main reducing agent for the silver ions. The shift of the position of the Fe K-edge absorption spectra represents one possibility to detect changes of the valence state of iron. Due to a changing number of screening electrons [12] this shift is directly related to the valence state. For the glasses used here, the oxidation of Fe^{2+} to Fe^{3+} was confirmed already as a result of Ag/Na ion exchange and subsequent thermal treatments [13]. This work shows the dependence of the Fe K-edge position on the duration of the ion exchange procedure. The results are represented in Fig. 4a and b. The data demonstrate a continuous increase with increasing duration of ion exchange up to approximately 400 h. Then, the oxidation seems to be completed. This assumption can be confirmed by the comparison to the data of crystalline references. Thus, the colouration of the glass, i.e., the formation of silver particles, and the oxidation of Fe^{2+} ions show an analogous dependence on the process time. That confirms the validity

of the redox reaction

$$Fe^{2+} + Ag^+ \rightarrow Fe^{3+} + Ag^0$$

It should be noted here that this charge transfer process requires the diffusion of silver ions and it is connected with structural rearrangements around the ions involved.

3.4. Formation of particles and characterization of their structure

In addition to the colouration of the glass sample discussed above, the presence of Ag nanoparticles of sizes ≥ 1 nm was revealed by TEM in samples ranging from 100 to 600 h ion exchange duration. However, a slight colouration could already be observed after 20 h. To investigate the nucleation of nano-particles and structural characteristics of species ≤ 1 nm in size additional experimental methods are required. Fig. 5 shows an example of a typical TEM image of ion-exchanged glasses. The dark image contrast of the metal particles within the disordered
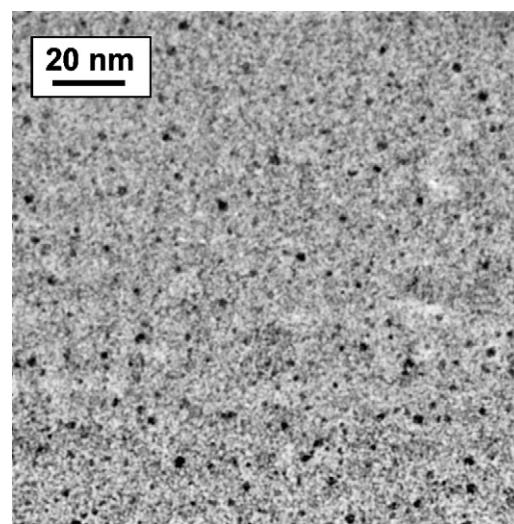

Fig. 5. TEM image of a glass sample containing Ag nanoparticles after 100 h ion exchange. This image represents the surface-near region.

glass matrix may clearly be seen. The particle size analysis by means of TEM gives a nearly constant mean size between 1.4 and 1.8 nm in the range of exchange durations of 100–400 h. This specific result must be discussed in more detail, and its reliability as well as the possible existence of further particles of different sizes should be checked by additional measurements. As long as the ion exchange does not result in a complete colouration of the glass that is upon about 500–600 h processing, there is no marked growth observed for the Ag nanoparticles of ≈1.5 nm in size. Only then, or upon thermal step processing, when probably also some changes in the glass matrix occurred, the mean particle size considerably increases to approximately 4 nm [14]. This size of Ag particles can be obtained likewise if the low-temperature ion exchange is performed together with a subsequent thermal treatment at elevated temperatures near the glass transformation temperature. In this temperature range the growth of crystalline precipitates is favoured above nucleation whereas at the lower temperatures used here (e.g. at 330 °C) precipitation processes are dominant.

Detailed investigations by TEM of particle formation in dependence on processing time and penetration depth showed a size distribution of Gaussian shape at depths near to the glass surface. This shape is accompanied by an asymmetric tail as shown in Fig. 6 for greater depths which is declining with the ion exchange progressing. For particles belonging to this tail no clear proof of only being composed of silver metal could be given, whereas otherwise the particles exhibit lattice plane fringes of crystalline silver in HREM images. Thus, it is assumed that the former particles represent an amorphous phase.
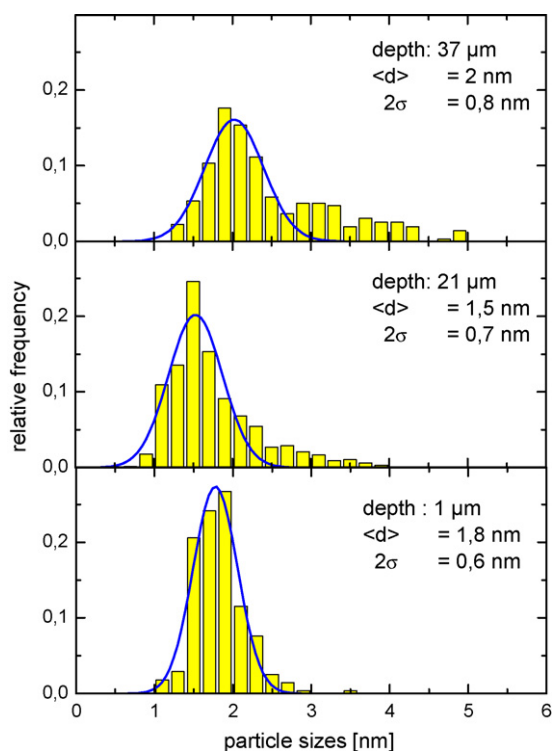

Fig. 6. Ag nanoparticle size distribution at different depths after 300 h: near the reaction front (37 μm), in the middle region (21 μm), near the sample surface (1 μm).
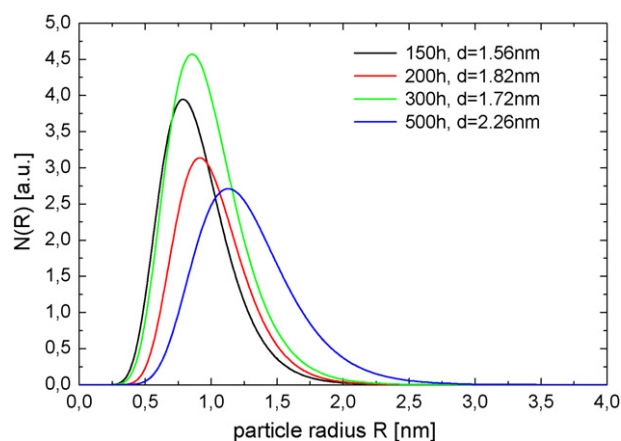

Fig. 7. Particle size distribution determined by SAXS for different process times.

The particles of this amorphous or metastable phase should contain subvalent argentic or argentous silver [14]. Their structure seems to be similar to crystalline silver oxides like Ag_6O_2 or silver silicates like Ag_5SiO_4 [15,16]. This was concluded on the basis of EXAFS investigations at the Ag K-edge, which revealed Ag–Ag bond lengths much less than that of the crystalline Ag lattice, for all ion-exchanged samples up to a process time of 400 h. This deviation disappears for extended durations of ion exchange (500–600 h) in the same way as the metastable species are dissolved. Therefore, the observed hindrance of particle growth should be caused by the formation of metastable Ag particles which are gradually transformed into the crystalline Ag structure after 500–600 h. Then, the particle growth is completed. With this assumption the results of both TEM and EXAFS experiments can be explained.

Finally, the results of small angle X-ray scattering carried out for 150, 200, 300 and 500 h ion exchange duration shall be discussed. The data were interpreted by fit using log-normal distributions of particle sizes. That yields mean sizes of 1.56–2.26 nm (see Fig. 7). The comparison with parameters of electron microscopy reveals a good agreement in the range of exchange durations of 100 to 400 h. Moreover, the estimated sizes of 2.26 nm for 500 h indicate the beginning of particle growth as it can be derived from TEM data after 600 h. Only the existence of larger metastable particles, as found in the asymmetric tail of sizes distributions determined by TEM, could not be confirmed by SAXS measurements. That means, their concentration should be comparably low.

4. Conclusions

The systematic investigation of Ag/Na ion exchange in soda-lime glasses with enhanced amounts of iron oxide demonstrates that at first the Ag ions diffuse into the glass matrix with a nearly constant interdiffusion coefficient. Then, they are reduced by Fe^{2+} ions as shown by XANES experiments and the formation of crystalline Ag takes place well below the glass transformation temperature. Thus, a reaction front is established which disappears at a duration of ion exchange of 600 h, i.e., when the sample is completely coloured. The increased interdiffusion

coefficient in the particles containing layer near the glass surface can not be explained by structural relaxations within the local environment of silver ions. Therefore, the course of concentration profiles is mainly affected by the absence or presence of Ag nanoparticles and corresponding structural changes in the respective glass region. The particle size depth profile shows nearly constant mean values in a certain distance from the reaction front and before penetration throughout the whole glass is completed. Near the reaction front an asymmetric tail of the size distribution can be found. The combination of TEM and EXAFS results indicates the formation of metastable particles like, e.g., argentous species. The disappearance of the reaction front by all-through colouration results in a recovery of the particle growth. This implies the conclusion that the metastable, silver containing precipitates were transformed into silver nanoparticles. That is accompanied by certain changes of the glass matrix structural properties. Nanoparticles or nuclei of sizes less than 1 nm could not be identified by means of the experimental methods used here. It will be the aim of future investigations to overcome this limitation.

Acknowledgements

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