Formation of silver nanoparticles in low-alkali borosilicate glass via silver oxide intermediates

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1. Introduction

Subsequent colouration of commercial glass by incorporation of noble metal particles of nanometre size has found considerable interest in materials research because of potential applications making use of their characteristic absorption [1–3]. The optical properties of such promising materials depend on concentration, size, shape, spatial arrangement and configuration of the nanoparticles in the glass matrix [4,5]. Conventional routes of processing like Na+/Ag+ ion exchange followed by heat treatment at temperatures below the glass transformation point Tg, resulting in the formation of silver oxide or silver metal nanoparticles, are widely employed for soda lime silicate glass (SLSG) [6,7] as well as alkali-rich borosilicate glass (BSG) [8,9]. A technologically remarkable modification of this process uses laser irradiation to achieve colour structuration on the micrometer scale of such glasses [10]. However, with BSG poor in alkali content (BSG 3.3), a transparent host of even higher chemical durability and thermal stability, such techniques failed up to now.

This behaviour is presumably caused not only by the low-alkali content of such glasses, but also by a high Ag+ stability [11]. Interestingly, it is in contrast to the behaviour of both types of glass with respect to silver doping to the melt. Silver oxide cannot be introduced into silicate glass in significant quantities by melting whereas this is possible with borate glass [12]. Colouration of silicate glass upon silver doping to the melt is widely suppressed, on the other hand, if high-field strength ions such as Al3+ are present in sufficient number [13]. The incorporation of alumina limits the number of non-bridging oxygens, and hence the reduction of silver ions, also in borosilicate glass [14]. Although there is clear experimental evidence [15,16], little is known up to now about precipitation of silver oxide species in glass on a nanometre scale as well as their transformation to Ag nanoparticles. Hulpus et al. [17] report on nearly micrometer-sized crystalline precipitates of Ag2O resulting from phase separation of the silver-lead borate glasses studied. At the surface of these silver oxide particles Ag nanoparticles are thought to form due to the reductive effect of lead ions. Similar effects of thermally induced formation of less than 1 nm thick layers of silver on Ag2O nanoparticles of 6–16 nm size have been reported by Banerjee et al. [18]. The heat treatment at 260–350 °C shifted the optical absorption band of these nanoparticles from a maximum position around 500 nm to one at about 450 nm. Nanoparticulate silver oxide AgOx materials are reported to exhibit characteristic chemical reversibility and phase transformation [19,20]. Because of its thermodynamical instability AgO decomposes into Ag2O at about 220 °C and to metallic Ag and O2 at around 410 °C [19]. Silver incorporated in GeO2 matrix was found to induce the formation of silver germanate upon heating to 500–600 °C which decomposes to form GeO2 and silver nanoparticles upon further heating [21].

Thermal decomposition leads to gradual changes of the relative composition of such materials, for example, from AgOx to Ag2O and Ag, during thermal processing where the transformation...
progresses from the surface of the oxide phase to the interior. Until now, no such details have been reported for similar processes occurring in silver doped glasses. In particular, the specific optical properties of the core-shell-like configuration of such particles have not been considered in detail. However, from experimental observations as well as calculations according to appropriate models it is known that a metal nanoshell around an oxide core causes a characteristic surface plasmon resonance (SPR) whose extinction maximum undergoes a distinct blue shift right to the corresponding position of spherical metal nanoparticles [22–24] when the shell configuration changes to a spherical one by inward-directed growth. Similar effects can be expected for reverse core-shell configurations, that is a metal core surrounded by an oxide shell [25] where a blue shift of the extinction maximum position occurs with decreasing shell thickness.

Within the frame of the present work we explored routes of chemical and thermal processing to achieve subsequent colouration of BSG 3.3 and thus to extend this technique to a technologically important material. The route finally found to be successful comprises silver doping by silver/sodium ion exchange below the glass transformation temperature followed by thermal processing well above, at 750 °C. The initial formation of silver oxide species may be understood in terms of a more general phase separation of borosilicate glasses affected by the incorporation of silver.

2. Experimental

The present study has been carried out with commercial BSG 3.3, namely Pyrex® of Corning, whose main components are 80.4 wt.% SiO2, 13 wt.% B2O3, 4.2 wt.% (Na,K)2O, and 2.4 wt.% A12O3. Thin glass platelets of about 12 mm × 16 mm in size were immersed in a molten mixture of AgNO3/NaNO3 containing 8 wt.% AgNO3 for Na+/Ag+ ion-exchange processing at 410 °C. Changes of the Fe2+/Fe3+ relation were monitored by optical spectroscopy using a PerkinElmer Lambda UV–vis spectrometer, as well as by quantitative electron spin resonance (ESR) measurements using a Miniscope MS 100 of MagnetTech working in the X band range of 9.3–9.6 GHz.

The colouration of the glass has been recorded using the above-mentioned PerkinElmer spectrometer. Depth-dependent extinction spectra by means of a microscope-spectrophotometer MPM 3 (Carl Zeiss) enabling to monitor changes of the optical extinction at different penetration depth beneath the glass surface have been taken from thin cross-sections of the samples as described in detail elsewhere [26,27].

3. Results and discussion

3.1. Incorporation of silver

A typical characteristic of BSG 3.3 is the small alkali content of 4–4.5 wt.% being essentially lower than that of typical SLSG and of alkali-rich BSG like BK7 of Schott (12–17 wt.%). Upon ion exchange and also subsequent annealing at temperatures below the glass transformation temperature Tc the samples remain colourless and do not exhibit any changes in the extinction spectra with respect to the as received glass. Neither for 2 h ion exchange at 410 °C, nor upon additional 12 h annealing at 480 °C any colouration can be observed, in contrast to the situation with SLSG where under comparable conditions distinct colouration effects occur [26]. This behaviour is probably influenced by the lower alkali content of BSG 3.3 which obviously affects the capacity for Ag+ upon ion exchange. The resulting total amount of incorporated Ag+ as measured by AAS is only about 1/100 of the Ag+ content that SLSG may include.

With respect to the colouration capability it has been reported that at not to high temperature low levels of alkali in excess of alumina do not introduce non-bridging oxygens into the glass network if compensated by boron oxide [14,28]. However, the presence of non-bridging oxygens is thought to play an important role either in Ag+ redox reactions making use of polyvalent ions as internal reductive where non-bridging oxygens may cooperate in short range charge transfer processes, or they even may serve themselves as charge donor for Ag+ reduction [29]. The deficiency of such species required for low-temperature processing suggested to explore the capabilities of a high-temperature heat treatment of silver-doped borosilicate glasses for colouration purposes, since from an evaluation of the Ag+ diffusion in the BSG 3.3 it is known that the Ag+ incorporation is not affected by principal diffusion restraints [26]. Thus an Ag+ containing region of about 20 μm depth formed upon 2 h ion exchange at 410 °C, that exhibits a concentration profile corresponding to a constant interdiffusion coefficient, could be transformed to a coloured, particles containing region of about 110 μm depth by subsequent annealing at 750 °C for 15 min [26,27]. That means, the narrow and steeply descending concentration profile due to the silver incorporation by ion exchange is greatly flattened out towards distinctly larger penetration depths upon high-temperature processing. Simultaneously, particles of varying configuration and optical properties are formed.

The total amount of metallic silver precipitated in this process considerably exceeds the reducing potential of polyvalent ions present the glass. As known from the technical product specification as well as spectroscopic investigation the glass contains about 100 ppm Fe2+ corresponding to 4.5 × 10−6 mol cm−3 which may serve as reductive. As proved by AAS measurements other reductives like As or Sb polyvalent ions can be excluded. The measured content of metallic silver near the surface approaches nearly 7 × 10−6 mol cm−3. Thus, a distinct part of the metallic silver formed must result from the decomposition of previously precipitated silver oxide species as will be discussed below. It can be assumed that at high enough temperatures this process is accompanied by a structural relaxation of the borosilicate matrix enabling a gradual removal of the oxygen from the particles containing glass region.

3.2. Colouration of the glass

The distinct yellow-brownish to brown colouration achieved upon 1 h annealing at 750 °C previously subjected to 2 h ion exchange at 410 °C is due to a broad extinction with a dominating band at about 490 nm (band I) accompanied by a shoulder at about 420 nm (band II) as shown in Fig. 1 [26,27]. This result is contrasting to the typical yellow colouration of SLSG due to silver nanoparticles [30–32]. Moreover, it does not represent a steady state, but distinct changes occur depending on the duration of thermal processing. The distribution of optical density among these two bands substantially changes with increasing duration of the heat treatment as it is shown in Fig. 1. Prolonged annealing leads to an almost complete decrease of the long-wavelength band I while simultaneously at the position of the short-wavelength shoulder a more and more dominating band II arises. Upon 10 h annealing only the latter is remaining with features characteristic for SPR of silver nanoparticles.
This behaviour is quite different from the evolution of colouration by Ag nanoparticles in SLSG where no such additional extinction, obviously due to intermediate particles of specific configuration as well as their transformation to Ag nanoparticles, has been observed. Depth-resolved spectrometry applied to this BSG 3.3 clearly reveals that the integral spectra cannot be interpreted straightforward, but must be considered as resulting from superimposition of various contributions of different depths [26,27]. As a first approach to this issue it may be supposed that band I, evolving as first result of the high-temperature processing, corresponds to subvalent oxidic silver species like Ag$_6$O$_2$ or Ag$_5$SiO$_4$ [33,34]. Both phases contain a certain portion of free charge carriers which may be responsible for the surface plasmon resonance observed as band I. Accordingly, it may be supposed that band II, evolving simultaneously with the decline of band I, is due to silver metal particles surrounded by a silver oxide shell. A reason for the rather fast decomposition of band I species could be their small thermal stability.

Similar effects on the position of absorption maxima may result from thermally induced refractive index changes in the very neighbourhood of embedded metal nanoparticles caused by inhomogeneous variations of the matrix composition or by chemical interaction with the surrounding matrix. This has been reported for silver in zirconia matrix [35] as well as for gold in silica matrix [36]. In both cases metal nanoparticles are considered to be present prior to thermal treatment, different from the case of metal incorporation in glass by ion exchange where metal oxide species are precipitated first [15–17]. Alternatively, a shift of the absorption maximum position corresponding to embedded metal nanoparticles may result where deviations from a spherical shape cannot be excluded. For silver nanoparticles in soda lime silicate glass of a few 10 nm size such effects may be achieved by thermomechanical processing leading to elongated particles with aspect ratios of about 2–4 [37,38]. However, the particle shape variations cannot be simply produced by annealing, but instead they tend to recede upon such treatment. Moreover, anisotropic shape evolution by growth processes is not known until now for metal nanoparticles in glass.

As soon as stable silver metal clusters are formed inside the above-mentioned intermediate particles during continued annealing, the surrounding oxide shell obviously tends to diminish. This corresponds to the evolution of position and shape of band II [26,27]. The successive transformation of these species into spherical silver nanoparticles is assumed to be finished only upon heat treatment of about 10 h duration. Only then a final state is achieved in all depths of the glass being represented by spherical Ag nanoparticles of various size. A more detailed analysis of the optical spectra, aimed at understanding the transformation process in more detail, will be given in a forthcoming paper which is intended to include also calculations according to appropriate models of composition and configuration of the particles as discussed above.
Fig. 4. Typical selected area electron diffraction pattern of one intermediate particle from 90 μm penetration depth upon 2 h ion exchange plus 1 h annealing at 750 °C.

After 10 h annealing at 750 °C the corresponding integral spectrum indicates that almost no intermediate species are present in the glass, although its rather broad long-wavelength tail needs some explanation. The optical density of the colouration achieved this way assumes values comparable to those usually obtained with soda lime silicate glass [30].

3.3. Structural characterization

By means of TEM and SEM in BSG 3.3 subjected to 2 h ion exchange at 410 °C and 1 h annealing at 750 °C nanoparticles have been found at penetration depths ranging from 15 to 700 μm. They exhibit a considerable variation in size, from 4.7 nm to about 200 nm, and concentration. At surface-near regions the nanoparticles have a size distribution of lognormal shape as shown in Fig. 2 for 60 μm depth. From the optical spectra it has been concluded that for this annealing time and at this depth the prevailing portion of nanoparticles should be present as intermediate species [26,27]. The relatively high image contrasts observed with these nanoparticles indicate that they must contain a high content of silver or even partly consist of metallic silver. This is also supported by an EDX analysis of typical intermediate particles of 30–40 nm in size using a spot of 100 nm² as it is shown in Fig. 3. Besides the silica constituents of the surrounding glass matrix mainly silver has been found. Obviously, the intermediate particles are not as stable towards electron irradiation as the silver nanoparticles obtained upon long term annealing at 750 °C. A certain degradation of intermediate phase particles upon exposure to the electron beam, such as changes in their appearance (irregular shape) and crystallinity (disordering), cannot be avoided.

In a few cases, single crystal electron diffraction patterns as the one shown in Fig. 4 for a particle at 90 μm penetration depth (1 h annealing at 750 °C) have been obtained using low dose illumination conditions. This diffraction pattern has been analyzed as being due to a single crystalline particle of cubic Ag₂O (lattice type cP6, space group Pn3m, no. 224) situated in (1 1 1) zone axis orientation. An example of a more close inspection of intermediate particles by TEM and HREM is shown in Fig. 5 for a particle at 90 μm penetration depth (1 h annealing at 750 °C). By varying image contrast the TEM image (Fig. 5(a)) clearly reveals its composition of different building units. From the Fourier-filtered representations of the diffractogram (FFT) of the corresponding HREM image (Fig. 5(b)) it can be noticed that different constituents having different lattice types are contained in this particle. However, they cannot be unambiguously related to the ion exchange and the thermal processing only, but a certain influence of electron beam-induced decomposition must be considered. From a larger number of HREM images like the one shown in Fig. 5, taken at 90 μm penetration depth (1 h annealing at 750 °C), the spacings of lattice plane fringes have been analyzed and the result is represented in Fig. 6(a) as distribution of lattice spacings with the maxima fit by Gauss curves. These maxima can satisfactorily be assigned to the spacings of the cubic Ag₂O lattice (cP6) as indicated by the corresponding Miller indices. Upon 10 h annealing at 750 °C the situation has completely changed as may be recognized from Fig. 6(b), where the distribution of lattice spacings resulting from an equivalent analysis at the same penetration depth (90 μm) exhibits only spacings of the face centred cubic lattice of silver.

From the structural characteristics as revealed by electron microscopy it can be concluded that, at the experimental conditions applied, a nanoparticulate composite of an oxidic silver phase in BSG is formed which contains already after 1 h anneal-
ing a noticeable component of metallic silver. There was no direct proof available of a subvalent silver oxide present in the glass, most probably because of its electron beam-induced degradation. For the same reason, no clear proof could be found for the configuration of particles formed upon thermal decomposition of the initially created intermediate phase species. With respect to the interaction of the electron beam with the glass samples or with constituent phases within the glass it can be stated that the HREM investigation using 400 kV accelerating voltage causes somewhat less damage. Therefore, the image contrast features of the particle shown in Fig. 5(a) certainly may be interpreted in terms of a silver particle surrounded by a not completely closed silver oxide shell. If the reason for this deviation from an ideal core-shell configuration of spherical shape can be found in electron beam effects or may be due to its thermal decomposition, is not crucial with regard to the assumed optical properties of a great number of such objects. In principle it can be assumed that during annealing silver oxide core-shell structures as discussed above transitonally may occur in the BSG. Oxide–metal core-shell nanostructures as well as reverse core-shell structures of metal cores surrounded by metal oxide shells have been reported repeatedly, in particular for silver-based materials and they are known to cause similar absorption behaviour in the visible range [18,21–25,40–42].

4. Conclusions

The colouration of low-alkali borosilicate glass upon silver/sodium ion exchange has been achieved by thermal processing at temperatures well above the glass transformation temperature. Optical spectroscopy and electron microscopy revealed that the formation of silver nanoparticles, proceeding on the reduction of incorporated ionic silver, includes the formation of silver oxide nanoparticles as intermediate stage. This process, accompanied by a characteristic absorption difference from that of the silver metal nanoparticles, is continued by a gradual transformation of the intermediates to Ag nanoparticles, starting at the very glass surface, and results in a depth-dependent variation of particle size and number density. Using this procedure optical densities fairly well comparable to those found in soda lime silicate glass are achieved. Application of laser irradiation instead of thermal processing, however, yields less intense colouration which is expected to be improved by employing a more appropriate irradiation technique for colour structuration.

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References