Synthesis and properties of sol-gel derived $AgCl_xBr_{1-x}$ colloid containing sodium alumo borosilicate glasses

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ABSTRACT

AgCl/AgBr crystallites with diameters of about 40 nm were synthesized within a sodium alumo borosilicate glass matrix by the sol-gel process. Ag was introduced into the sol through the addition of an ethanolic $AgNO_3$ solution. After gelation, $AgCl_xBr_{1-x}$ was generated by treating the gel with NaCl and CuBr solutions. The gel can be densified to a glassy powder that shows a darkening effect with a saturation behaviour after UV irradiation and recovers at elevated temperatures (≥ 150 °C). The best recovery kinetics were obtained for a silver halide content of about 12 μmole/g.

1. INTRODUCTION

Silver halide containing photochromic glasses made from melts have extensively been investigated since the first publication by Armistead and Stokey[1-3] in 1964. In these glasses, the photochromic phase is based on Ag halides which is generated by phases separation from homogeneous glasses. The alternative route, to synthesize the two phases separately would open new possibilities for independent matrix and active phase tailoring. The sol-gel process is considered to be an interesting way to tackle this goal. This process is an interesting low temperature route alternative to the melting technique and a new glass composition could be synthesized not accessible via melting[4]. The sol-gel process can be used for the synthesis of multicomponent glasses with good homogeneity and purity[5] and for controlled doping of glasses with inorganic as well as organic components such as photochromic molecules[6].

The photochromic effect in inorganic glasses depends strongly on glass composition[7,8] and structural parameters[9] (e.g. crystallite size), but there are still some open questions concerning the mechanism.

Since the sol-gel synthesis of glass differs completely from the melt synthesis, the first question to be answered is, whether it is possible to generate photochromic Ag halide phases or not by this route, and which synthesis parameters have to be employed. Therefore

this paper is mainly focused on the development of preparation techniques for introducing photochromically active Ag halides into sol-gel derived glasses and to prove the photochromic effect.

2. EXPERIMENTAL

The sol representing a composition in the system $SiO_2/B_2O_3/Na_2O/Al_2O_3$ was synthesized by dissolving 0.595 mole tetraethoxysilane in ethanol and stirring it at room temperature for 30 minutes with nitric acid as catalyst. The resoluting sol was then heated up to 50 °C and 0.205 mole trimethylborate was added dropwise. After stirring for two hours the solution was cooled to room temperature and 0.095 mole aluminaisopropoxide, dissolved in ethanol and water, was added. After stirring for 30 minutes the sol was cooled down to 0 °C and 0.105 mole sodiummethoxide was added.

Silver was introduced by addition of ethanolic $AgNO_3$ solutions in varying concentrations to obtain Ag contents from 0.00016 M to 0.048 M in the sol. The Ag containing sols gelled after 10 minutes at 50 °C and were treated for 10 hours at 60 °C and dried for 4 hours at 80 °C (uncovered). After that the gels were grinded to fine powders.

For loading with Cl and Br, the powders were infiltrated with an aqueous 0.1 M sodium chloride solution for 12 hours. After filtering and drying the process was repeated with 0.02 molar solution of CuBr. Afterwards for densification the powders were heated up to 640 °C for 3 hours.

For investigation of the photochromic effect, the glass powders were irradiated with a 500 W xenon lamp using a cooled sample holder at a distance of about 30 cm from the lamp. Crystalline precipitates in the dried gel powders and the glass powders were investigated by x-ray diffraction.

3. RESULTS AND DISCUSSION

3.1. Optical properties of the sols

The first interesting observation during the sol-preparation was the spontaneous color change of the sodium alumo borosilicate sol on the addition of the $AgNO_3$ solution. The sols turned to yellow, orange or brown immediately after $AgNO_3$ addition, depending on the silver concentration. The UV/VIS spectra of these sols are shown in fig. 1. They show three bands with a sharp peak between 225 and 235 nm, peaks between 260 and 280 nm and smaller broad absorptions (about 250 nm half band width) between 390 and 420 nm wavelength. The spectrum of the silver-free sol that has an absorbance edge at

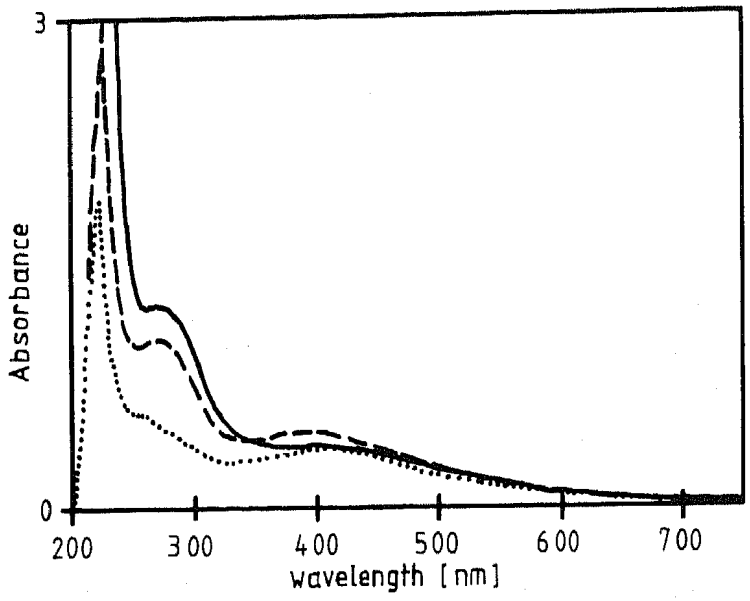

Fig. 1. Optical absorption spectra of sodium alumo borosilicate sols with different Ag content: 0.048 M (——), 0.008 M (---), 0.0032 M (...).

about 240 nm is already subtracted. The formation of similar absorption is reported from silver metal colloids by Linnert et al.[10] produced by Co^{60}-radiolysis of Ag compounds in alcoholic solutions. He concluded that absorption bands at shorter wavelengths than the plasmon band of metallic silver colloids (around 380 nm) can be attributed to very small silver clusters having non metallic properties. The peak at 275 nm he attributed to Ag_4^{2+} clusters. In[11-13] it was shown that small metallic silver colloids (1 to 3 nm in diameter) in glasses show peaks between 410 and 425 nm with broad half band widths (about 100 nm), so that the resulting absorption spectrum may have much larger half band widths in case of colloids with larger size distribution.

From these results, one can conclude that in the investigated sol-gel system very small silver clusters (peaks at about 230 nm and about 270 nm) are formed spontaneously together with small metallic silver colloids with a relatively large size distribution (peaks at about 400 nm). Due to the short life time of the clusters and colloids of only several hours, no investigations with electron microscope were possible.

The mechanism of formation of the non-metallic silver clusters and metallic silver particles in our system is the subject of the forthcoming papers.

3.2. Properties of gels

The interesting result of the formation of small Ag clusters rose the question whether these particles can be used as nuclei for the halide formation or even can be transformed to halides preserving the size or average number of silver atoms per particle. In order to investigate this, it was necessary to increase the gel formation rate to trap the colloids within the gel before they destabilized. This was achieved by increasing the temperature slowly to 50 °C. Transparent gels showing the same colors as the sols were obtained.

In order to characterize the state of the silver in the dried gel powders reflectance measurements were carried out and were converted into the Kubelka-Munk function[14] (KM). The value of the KM was considered to be proportional to the absorption coefficient in the range between 360 to 740 nm, first, because the reflectivity of a silver-free gel powder was found to be constant in first approximation in this range and second, it can be assumed that the scattering behaviour of the gel powder is not changed remarkably by the incorporated particles. Below 360 nm, the reflectivity changes remarkably, therefore KM spectra are only discussed between 360 and 740 nm. KM spectra of low silver content type powders (2.2 μmole/g) showed absorption between 360 and about 600 nm, but a quantitative evaluation is difficult with respect to their low KM values (below 0.1).

Fig. 2 shows KM functions of the high silver content powders. The absorption peaks at 410 nm have relatively large half band widths (as already known from small silver colloids in glasses).

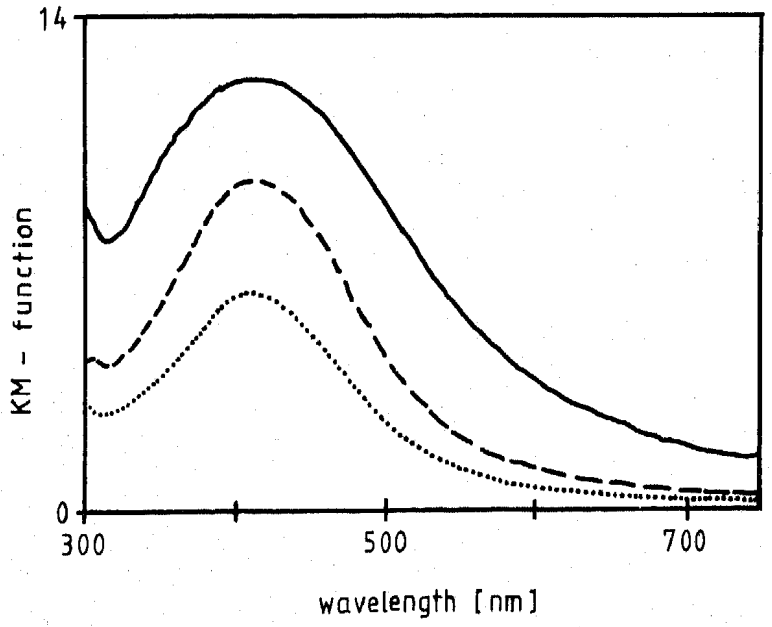

Fig. 2. Kubelka-Munk functions of dried gels with different Ag content with respect to the original sol: 0.048 M (——), 0.016 M (---), 0.008 M (...).

Since preliminary darkening test, carried out with different Ag halide contents, showed that the fastest darkening kinetics were obtained with medium Ag concentrations (around 9 μmole Ag/g gel), TEM investigations were carried out with these samples (before densification to glasses). The electron micrographs show the presence of metallic silver colloids (identified by electron diffraction pattern). Quantitative analysis of the micrographs by image processing led to the result that 93 % of the particles have diameters below 1.7 nm. The gels did not change their color when storing in air and light for weeks.

After infiltration with NaCl solution and before infiltration with CuBr solution sharp peaks attributed to silver chloride particles appeared in x-ray diffraction spectra for powders with medium and high silver concentrations. Particle diameters between 38 and 47 nm with an average error of about 2 nm were calculated from the half band width of the most intensive peak at 2 θ = 32.2° using the Scherrer equation[15]. It is obvious, that the particle sizes of the AgCl crystallites are substantially larger than those of the silver colloids. This has to be attributed to a particle growth mechanism, probably taking place during the oxidation step from Ag° to Ag^+, based on the AgCl formation as the thermodynamic driving force for the oxidation step. A dependence of the particle size on the silver concentration could not be observed, but 50 nm seemed to be the upper limit of the particle size, suggesting a pore size controlled particle growth. After Br^- treatment, the samples were investigated by x-ray again. The powders show only sharp peaks with positions between AgCl and AgBr (nearer to bromide than to chloride) suggesting a mixed crystal phase of $AgCl_xBr_{1-x}$.

The photochromic behaviour was investigated after heating the powders to 640 °C. All powders darkened by UV irradiation. Samples with high silver content also darkened in daylight. In Fig. 3 the spectra of irradiated glass powders using the KM approach as described above (spectrum of the unradiated powders are subtracted) are shown. A broad absorption occurs with a maximum between 550 and 600 nm. The absorption curve of the high Ag content glass powder shows some similarity at 500 to 600 nm to spectra of Cu doped irradiated AgCl as described in reference[3].

Using the mean KM value between 500 and 650 nm wavelength (according to the spectral sensitivity of the human eye) as a measure for the darkening a saturation level is reached in all samples after irradiation for 15 to 25 minutes. The level increases with increasing Ag concentration. The half saturation value is reached within the first minute of irradiation. This is in the same range as obtained in photochromic glasses made from melts[2].

The darkened samples did not recover at room temperature. To obtain complete recovering of the sol-gel photochromic glass powders, temperatures ≥ 150 °C had to be used. In order to obtain a survey over the recovering behaviour, thermal treatments were performed by

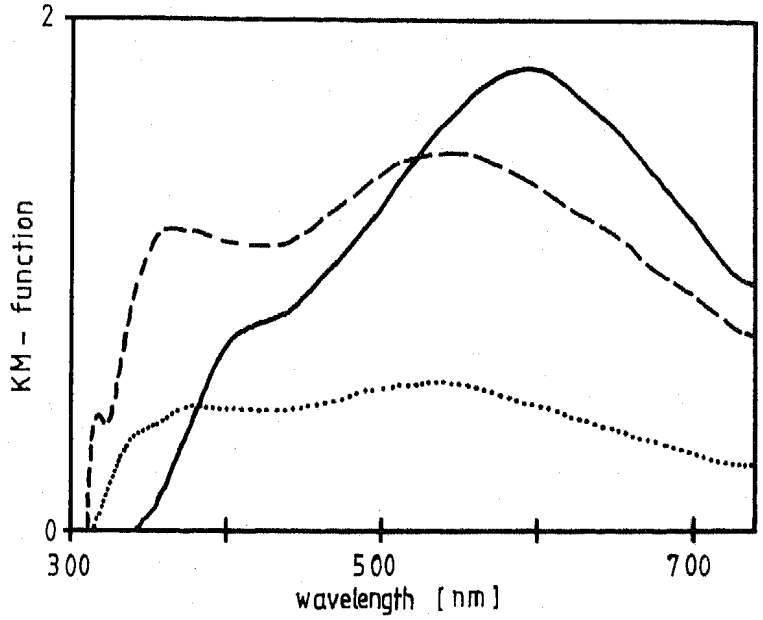

Fig. 3. KM-functions of irradiated glass powders until the absorbance saturated. These glass samples were obtained after the heat treatment of the dried gels presented in Fig. 2.

heating the samples at different temperature as indicated in fig. 4 (accumulated temperature treatment for one hour). The KM value is plotted versus the temperature of the thermal treatment. The samples with the highest Ag content start to recover at 100 °C, and at 250 °C, the 50 % saturation level is reached. All the other samples show

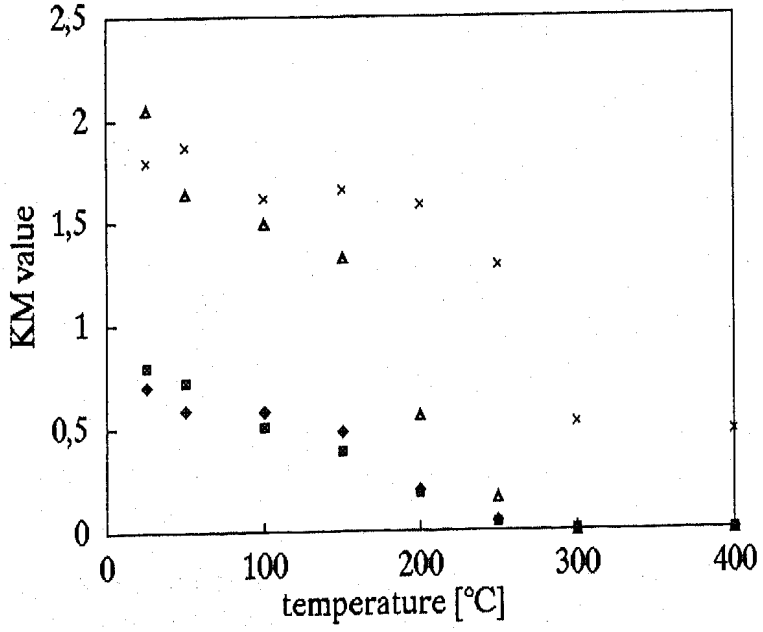

Fig. 4. Change in the mean KM value of irradiated glass powders with different silver contentions in the original sol: 0.0032 M (■), 0.008 M (◊), 0.016 M (Δ), 0.048 M (x)

better recovery kinetics, because recovery starts already at 50 °C and the half saturation value is achieved at temperatures between 150 and 170 °C. The sample with medium Ag concentration of about 12 μmole/g has the best thermal bleaching kinetics. After irradiation for 5 minutes (63 % saturation) it is completely colorless after thermal treatment at 150 °C. Samples with lower Ag content need 300 °C for complete recovery and the absorbance in the darkened state is too low to be of practical interest.

4. CONCLUSIONS

The experiments have clearly shown that by use of the sol-gel route it is possible to synthesize a glassy material with photochromic behaviour based on Ag halides. This is obtained by generation of small silver clusters and colloids in the sol, subsequently trapped in the matrix by the gelation step. The formation of the Ag colloids in solution seems to be of high importance for the formation of Ag halide crystals of proper sizes. The Ag colloids are considered to act as nuclei for the Ag halide formation. The photochromic behaviour of the densified glass powders is not clear with respect to their mechanisms and the kinetics need further optimization, but it could be shown, that the sol-gel process opens an interesting new route to photochromic glasses.

5. ACKNOWLEDGEMENTS

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