

# In Situ EXAFS and TEM Investigations of Ag Nanoparticles in Glass

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**Abstract.** Ag particle-glass composites produced by ion exchange processes of soda-lime glasses were investigated by EXAFS spectroscopy at the Ag K-edge. The spectra measured at 10 K were used to characterize the structure of nanoparticles as a result of ion exchange. The evolution of Ag K-edge EXAFS oscillations measured by in situ heating at 823 K as a function of time clearly shows an increase of Ag-Ag distance and coordination number caused by annealing. Together with transmission electron microscopy characterization a preferred growth of Ag particles with respect to nucleation has been found that leads to increased particle sizes in deeper glass regions.

**Keywords:** EXAFS, nanoparticle, glass, electron microscopy.

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## INTRODUCTION

Glasses containing metal nanoparticles are of long-term interest, not only because of the simple handling for colouration, but also as their specific optical properties can be adjusted through the mean particle size and the corresponding size distribution (see, e.g., [1]). Generally, such particle-glass composites can be produced in different ways including Na<sup>+</sup>/Ag<sup>+</sup> ion-exchange and ion implantation, where the first one is the most common route. In the case of iron oxide containing glasses the formation of Ag nanoparticles upon ion exchange results from the reduction of ionic Ag<sup>+</sup> by Fe<sup>2+</sup> ions followed by nucleation and growth. To enable deeper insight into the elementary processes of particle formation with the aim to introduce specific linear and non-linear optical properties into the glass, *in situ* EXAFS studies of Ag nanoparticles in glass were performed at elevated temperatures. Since EXAFS data only allow determination of integral structural parameters, without local information concerning individual nanoparticles, transmission electron microscopy (TEM) investigations were additionally carried out.

## EXPERIMENTAL

Ag particle-glass composites were produced by ion exchange of slices, 15mm×15mm in square and about 150 μm thick, of soda-lime glass with 1.8 % Fe<sub>2</sub>O<sub>3</sub> in a

NaNO<sub>3</sub>/0.05 % AgNO<sub>3</sub> melt at 603 K for 195 h. In HASYLAB at beam line X1, Ag K-spectra (25.514 keV) were recorded in transmission mode at 10 K by means of a liquid-helium vapour flow cryostat, where a laboratory-made oven was utilised for 8 h *in situ* heat treatment at 823 K. To achieve sufficient high signal intensity, a stack of several glass slices was used as a sample. EXAFS data processing was done using the UWXAFS program package [2] with the theoretical amplitude and phase functions calculated by FEFF 7. Before any heat treatment, Ag K-spectra were taken as reference from the as-prepared glass (sample A) at 10 K. The evolution of the Ag K-edge EXAFS oscillations as a function of time (see Fig. 1), when the sample was kept at 823 K, clearly shows structural changes caused by annealing. After this heat treatment X-ray absorption spectra at the Ag K-edge were additionally recorded from the annealed sample (B) at 10 K for comparison.

For the TEM investigation electron-transparent cross-section specimens were prepared in the usual way. Energy-dispersive X-ray spectroscopy of such a cross-section of the as-prepared sample showed that the silver content decreases continuously from each surface side down to a depth of about 50 μm. Here, deep in the glass interior no silver could be detected, while upon annealing a certain amount of silver was found throughout the whole sample pointing to its inward diffusion. Microstructural characteristics of the glasses were investigated by TEM using a Philips CM 20 FEG at 200 kV.

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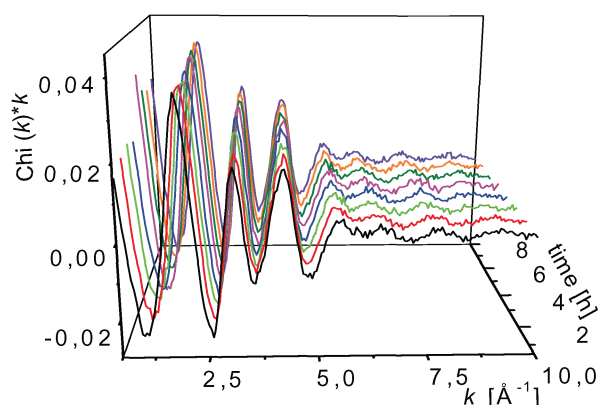
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## RESULTS AND DISCUSSION

### EXAFS Data

Fourier transforms of EXAFS oscillations obtained from both the as-prepared and the annealed sample, at 10 K, and corresponding fits are given in Fig. 2. Fit results show that for the as-prepared sample the nearest Ag-Ag distance  $R$  amounts to 2.85 Å at 10 K, the coordination number  $N_{\text{Ag-Ag}}$  is about 3.1 and the Debye-Waller factor ( $DWF$ ) is 0.0040 Å<sup>2</sup> (the respective values of bulk silver are:  $R = 2.88$  Å,  $N_{\text{Ag-Ag}} = 12$ ,  $DW = 0.0027$  Å<sup>2</sup>). The Ag-Ag distance of the 1st coordination shell is slightly reduced with respect to bulk silver, which is well known from such nanoparticles embedded in a matrix and can be explained by remarkable contributions of silver atoms located within the surface region of the particles as well as by the existence of silver containing clusters within the glass. Such clusters should have a structure similar to that of crystalline Ag-O compounds [3]. The presence of a great number of predominantly small Ag species is also reflected by the higher Debye-Waller factor, representing a higher static disorder caused by the increasing portion of surface atoms. It should be noted here that EXAFS is sensitive to contributions of Ag clusters and particles of all sizes in contrast to TEM investigations.

After 8 hours of heat treatment, the parameters of the nanoparticle-glass composite have changed to  $R = 2.88$  Å,  $N_{\text{Ag-Ag}} = 6.2$  and  $DW = 0.0035$  Å<sup>2</sup>, indicating on the whole a more distinct Ag-Ag neighborhood. That means that the Ag-Ag distance is approximately the same as that for bulk material. The coordination number increases strongly. That indicates, together with the measured Ag-Ag bond length, a drastic in-



**FIGURE 1.** Evolution of EXAFS oscillations at the Ag K-edge during in situ annealing for 8 h at 823 K.

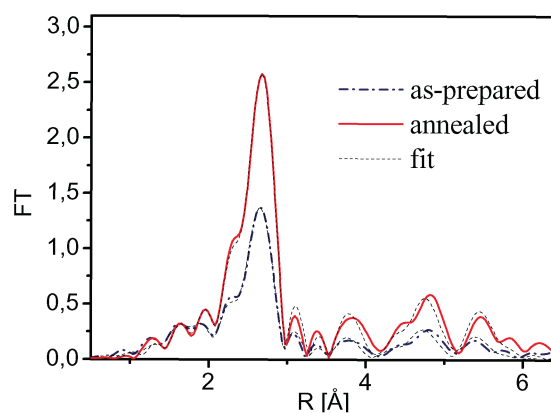
crease of the size of Ag nanoparticles. Thus the bond length contraction vanishes. However, the Debye-Waller factor is only slightly reduced. Therefore, a certain amount of small Ag clusters or particles must still be considered.

Additional information comes from the EXAFS data of Ag-O correlation. It is well known that the silver ions occupy a twofold oxygen environment, as a result of ion exchange, with an Ag-O distance of approximately 2.15 Å [4]. Our data show that one part of the silver species is reduced to neutral silver atoms already before annealing. That explains the value of the Ag-O coordination number less than two (see Table 1). Its further decrease upon thermal processing indicates the additional reduction of silver ions during this treatment. That could result in the formation of new nuclei of Ag particles and/or the growth of existing nanoparticles.

The data of *in situ* EXAFS experiments at 550°C confirm the increase of Ag-Ag coordination number as well as a slight increase of the corresponding bond length. The evaluation of these data shows that the mean size of the larger particles grows. This process can be described by diffusion of Ag ions towards existing particles and their subsequent reduction. Furthermore, it can be assumed that the additional particles detected by TEM are formed by the growth of stable nuclei.

### TEM Investigations

Typical TEM bright-field images taken from different depths of the as-prepared and the annealed sample show that an increased number of Ag particles is present upon annealing in comparison to the initial state. For both samples, similar values of the particle



**FIGURE 2.** Fourier transforms obtained from the as-prepared and annealed sample, respectively, at 10 K and corresponding fits.

**TABLE 1.** EXAFS parameters obtained from the as-prepared and annealed sample, respectively, at 10 K

Sample	Ag-Ag distance [Å]	DWF Ag – Ag [Å <sup>2</sup> ]	Ag-Ag Coordination number	Ag-O Distance [Å]	DWF Ag – O [Å <sup>2</sup> ]	Ag-O Coordination number
As-prepared (sample A)	2.8538 ±0.0052	0.0040 ±0.0008	3.6 ±0.5	2.1660 ±0.0264	0.0018 ±0.0061	0.7 ±0.3
Annealed (sample B)	2.8811 ±0.0014	0.0035 ±0.0002	6.2 ±0.2	2.1622 ±0.0183	0.0001 ±0.0032	0.4 ±0.1

size was measured in surface-near regions (A: 1.5-6.5 nm, B: 1.5-5 nm). These sizes are not available from EXAFS data of Ag-Ag coordination because of the existence of isolated Ag ions inside the glass matrix. However, significant differences in the area density of nanoparticles can be observed, in the case of sample A it amounts to approximately  $4.8 \cdot 10^{15} \text{ m}^{-2}$ , whereas it even is about  $1.6 \cdot 10^{16} \text{ m}^{-2}$  for B. Presumably, the thermal treatment predominantly promoted nucleation processes, thus leading to an increase of the number of particles. However, EXAFS parameters, especially the Debye-Waller factor, do not support this assumption. Generally, for both samples, the mean particle size increases as a function of depth. In addition, in the case of the as-prepared state the number of Ag particles drops down drastically in regions deeper than about 50  $\mu\text{m}$ . In the centre of this sample nearly no particles are present. This is in contrast to the annealed sample that exhibits a few particles with sizes up to 30 - 40 nm besides a lot of smaller ones in its central region. The occurrence of an increased number of Ag particles throughout the whole sample combined with the existence of relatively large particles explains why the 1st shell Ag-Ag distance of 2.88 Å, which is similar to that of bulk material, has been found for the annealed sample by EXAFS.

## CONCLUSIONS

The combination of EXAFS spectroscopy and TEM examination enables a detailed description of elementary processes of the formation of Ag nanoparticles in glass. Owing to the heat treatment at 550 °C silver ions diffused into interior regions. Thus

Ag particles with of 3 nm mean size are formed near the very surface, whereas a bimodal size distribution appears in the centre with sizes up to 40 nm.

TEM analysis showed an increase of number and size of particles as well as their spreading into the central region of the glass. As revealed by the nearly constant Debye-Waller factor, however, the growth of Ag nanoparticles is more preferred than nucleation of new ones. This supports the assumption that most of the particles detected by TEM after annealing have already existed before in the form of nuclei or clusters invisible for TEM inspection because of their too small a size of less than 1nm.

Efforts are in progress now to use the *in situ* EXAFS data for a description of the kinetics of particle growth.

## ACKNOWLEDGMENTS

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## REFERENCES

1. R. E. Hummel and P. Wissmann, *Handbook of Optical Properties II: Optics of Small Particles, Interfaces and Surfaces*, Vol. 2, , CRC, New York, 1997.
2. S.I. Zabinsky, J.J. Rehr, A.L. Ankudinov, R.C. Albers, M.J. Eller, *Phys. Rev. B* **52**, 2995 (1995).
3. M. Jansen, *Angew. Chem.* **99**, 1136 (1987).
4. M. Dubiel, S. Brunsch, S. Kolb, D. Gutwerk, H. Bertagnolli, *J. Non-Cryst. Solids* **220**, 30 (1997).