

# XAFS Studies of Silver Environments in Ion-Exchanged Glasses

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**Abstract.** The X-ray absorption fine structure (XAFS) technique was used to analyze the structural geometry of Ag atoms introduced into soda-lime silicate glass and soda aluminosilicate glass by ion-exchange methods. The results show that Ag<sup>+</sup> ions in aluminosilicate glass are coordinated by about two oxygens and the nearest-neighbor Ag-O distance increases when the Ag<sup>+</sup>-for-Na<sup>+</sup> ion-exchange ratio is larger than 0.47. When the exchange ratio is low, the introduced Ag<sup>+</sup> ions are stabilized at the non-bridge oxygen (NBO) site with a Ag-O distance of 2.20 Å, and the Na<sup>+</sup> ions in the AlO<sub>4</sub> site are exchanged by Ag<sup>+</sup> ions after full replacement of the NBO sites with a Ag-O distance of 2.28 Å. The disorder of Ag-O coordination increases with increasing ion-exchange ratio in aluminosilicate glass where Ag<sup>+</sup> ions are coordinated by NBO and bridge oxygen (BO).

**Keywords:** Glasses, silver atoms, structural environment, XAFS

**PACS:** 61.10.Ht, 61.46.+w, 81.05.kf

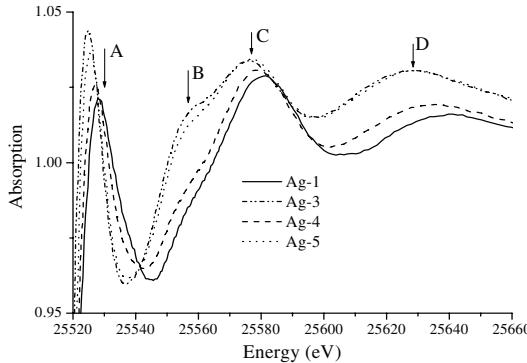
Recently, the preparation and characterization of Ag-doped glass composites has been further stimulated by its peculiar optical properties, especially an increased third-order susceptibility, making such glass a promising candidate for application in integrated optics and photonics [1-3]. Ag<sup>+</sup> for Na<sup>+</sup> ion-exchange is an easy and important method to introduce Ag<sup>+</sup> ions into glasses as a first step to obtain Ag nanoparticle-glass composites [4-6]. For Ag<sup>+</sup> for Na<sup>+</sup> ion-exchanged glass, Na K-edge extended x-ray absorption fine structure (EXAFS) analysis revealed that Na ions take a large coordination number (CN) of 6.4-7.6 with a Na-O distance of 2.60-2.61 Å at NBO (non-bridge oxygen) site and 5.1-6.4 with a Na-O distance of 2.61-2.62 Å at AlO<sub>4</sub> ( $\text{O}_4$  represents the bridging oxygen) in silicate and aluminosilicate glasses [7]. Ag K-edge EXAFS analysis on Ag<sup>+</sup> for Na<sup>+</sup> ion-exchanged silicate and aluminosilicate glasses showed that Ag<sup>+</sup> ion has a CN of 2.1 with a Ag-O distance of 2.08 Å at NBO site and a CN of about 2.5 with a Ag-O distance of 2.23 Å at AlO<sub>4</sub> site [8]. Due to a large decrease of CN by the replacement of Ag<sup>+</sup> for Na<sup>+</sup> ions, a large relaxation of local-structure would be induced at NBO and AlO<sub>4</sub> sites. Yano *et al.* [9] found that when the ion-exchange ratio was low, the introduced Ag<sup>+</sup> ions were stabilized at the non-bridge oxygen sites, and the Na<sup>+</sup> ions in AlO<sub>4</sub> sites were exchanged by Ag<sup>+</sup> ions after full replacement of NBO sites. In this article, silver structural environments in

soda aluminosilicate glass and soda-lime silicate glass were studied by x-ray absorption fine structure technique.

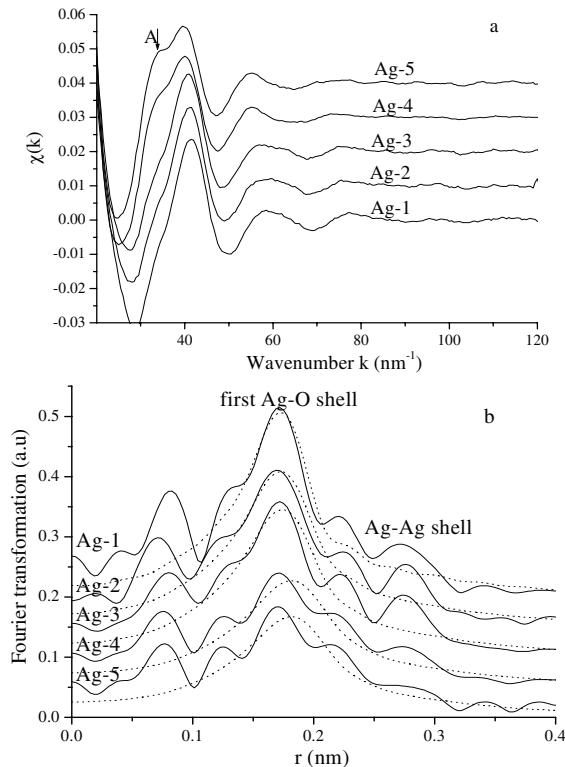
In this research, samples Ag-1, Ag-2, Ag-3, Ag-4 and Ag-5 with different ion-exchange ratio  $x = \text{Ag} / (\text{Ag} + \text{Na})$  of 0.24, 0.38, 0.47, 0.68, and 0.95, respectively, were prepared by soaking 20Na<sub>2</sub>O-10Al<sub>2</sub>O<sub>3</sub>-70SiO<sub>2</sub> (mol%) glass samples (10 × 15 × 0.3~0.4 mm) into a fused salt bath of 48Ag<sub>2</sub>SO<sub>4</sub>-52AgCl (mol %) at 400°C for 15 min ~13 h. In order to decrease the concentration gradient, the sample was held at the same temperature in an ambient atmosphere. The soda-lime glass slides with a composition of 13.3Na<sub>2</sub>O - 0.31K<sub>2</sub>O - 8.69CaO - 4.15MgO - 0.87Fe<sub>2</sub>O<sub>3</sub> - 0.59Al<sub>2</sub>O<sub>3</sub> - 72.09SiO<sub>2</sub> (wt %) were immersed in a molten mixture of NaNO<sub>3</sub> and 0.05 wt% AgNO<sub>3</sub> held at 330°C for 192 h (Ag-6). After cleaned in deionized-water and ethanol, the ion-exchanged samples were subjected to thermal processing in air at 480°C for 7 h (Ag-7).

Ag K-edge (25514 eV) x-ray absorption fine structure spectra were measured at beamline X1 of HASYLAB (Hamburg, Germany) in transmission mode, utilizing a Si (311) double-crystal monochromator. Measurement temperature was kept at 12K by using a liquid helium vapor flow cryostat equipped with an electric heater. The energy resolution of the experiments,  $\Delta E/E$ , was about  $2.5 \times 10^{-4}$ . Harmonic rejection was achieved by detuning the

monochromator crystals between 40% and 50%. The software package UWXAFS 3.0 [10] was used to obtain structural parameters such as coordination number N, interatomic distance r and Debye-Waller factor  $\sigma^2$ . EXAFS oscillation,  $\chi(k)$  was extracted from the raw Ag K-edge x-ray absorption. The  $\chi(k)$  oscillation was weighted by  $k^2$  and subsequently Fourier-transformed into real space using a Hanning window function. The uncertainties of coordination number, interatomic distance and Debye-Waller factor are  $\pm 0.5$  atom,  $\pm 0.01 \text{ \AA}$  and  $\pm 0.005 \text{ \AA}^2$ , respectively.



**FIGURE 1.** Ag K-edge x-ray absorption fine structure spectra of different samples.

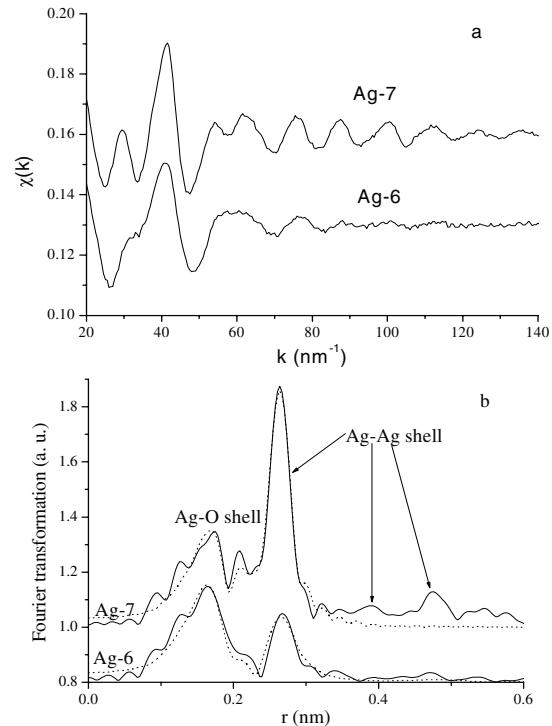


**FIGURE 2.** (a) Ag K-edge EXAFS spectra, and (b) the corresponding Fourier transforms of samples Ag-1, Ag-3, Ag-4 and Ag-5. Dot curves are fits calculated by UWXAFS 3.0.

Figure 1 gives the Ag near K-edge x-ray absorption spectra of samples Ag-1, Ag-3, Ag-4 and Ag-5. It shows that distinct differences are observed in the near-edge absorption spectra when the ion-exchange ratio x is more than 0.47, indicating that the structural environment of Ag changes when ion-exchange ratio x exceeds this value.

Figure 2 shows Ag K-edge EXAFS spectra and the corresponding Fourier transforms of samples Ag-1, Ag-2, Ag-3, Ag-4 and Ag-5. The difference in the EXAFS spectra marked as A appears when the ion-exchange ratio x is more than 0.47. Fourier transforms indicate that the amplitude of the first Ag-O shell is reduced gradually with increasing  $\text{Ag}^+$  for  $\text{Na}^+$  ion-exchange ratio.

Figure 3 gives the Ag K-edge EXAFS spectra and the corresponding Fourier transforms of samples Ag-6 and Ag-7.



**FIGURE 3.** (a) Ag K-edge EXAFS spectra and (b) the corresponding Fourier transformations of samples Ag-6 and Ag-7. Dot curves are fits calculated by UWXAFS 3.0.

Figure 3 indicates that there are two structural environments for Ag atoms in samples Ag-6 and Ag-7: Ag-O coordination and Ag-Ag coordination. The amplitude of the Ag-Ag shells is larger in sample Ag-7 than in sample Ag-6. The existence of Ag-Ag shells indicates the formation of Ag clusters in soda-lime silicate glass during  $\text{Ag}^+$  for  $\text{Na}^+$  ion-exchange, and subsequently thermal treatment induces further growth of Ag clusters.

**TABLE 1.** Structural parameters obtained from fits using the UWXAFS software package.

Sample	Fitting range		Nearest-neighbor Ag-O coordination			Nearest-neighbor Ag-Ag coordination		
	$\Delta k$ ( $\text{\AA}^{-1}$ )	$\Delta r$ ( $\text{\AA}$ )	R ( $\text{\AA}$ )	$\sigma^2$ ( $10^{-3} \text{\AA}^2$ )	N	r ( $\text{\AA}$ )	$\sigma^2$ ( $10^{-3} \text{\AA}^2$ )	N
Ag-1	3-12	1-3	2.19	7.2	1.5	---	---	---
Ag-2			2.20	10.4	1.6	---	---	---
Ag-3			2.21	10.8	1.6	---	---	---
Ag-4			2.28	14.4	1.6	---	---	---
Ag-5			2.28	14.6	1.6	---	---	---
Ag-6	3-14	1-3	2.14	6.7	1.6	2.81	10.9	1.8
Ag-7			2.14	4.8	1.3	2.881	5.0	2.5

Table 1 gives the structural parameters obtained from the fits using the UWXAFS software package. From Table 1, it is found that the  $\text{Ag}^+$  ion in soda aluminosilicate glass is coordinated by about two oxygen and the Ag-O distance increases when the  $\text{Ag}^+$  for  $\text{Na}^+$  ion-exchange ratio is larger than 0.47. When the exchange ratio is lower than 0.47, the introduced  $\text{Ag}^+$  ions are stabilized at the non-bridge oxygen sites with a Ag-O distance of about 2.20  $\text{\AA}$ , and the  $\text{Na}^+$  ions in  $\text{AlO}_4$  sites are exchanged by  $\text{Ag}^+$  ions after full replacement of NBO sites with a Ag-O distance of 2.28  $\text{\AA}$ . The disorder in the Ag-O coordination increases with increasing ion-exchange ratio in soda aluminosilicate glass where  $\text{Ag}^+$  ions are coordinated by NBO and BO.  $\text{Ag}^+$  ions are coordinated by NBO with a Ag-O distance of 2.14  $\text{\AA}$  in soda-lime silicate glass, and the order of Ag-O coordination is higher in soda-lime silicate glass than in soda aluminosilicate glass. Ag-Ag nearest-neighbor distances in samples Ag-6 and Ag-7 are 2.81  $\text{\AA}$  and 2.88  $\text{\AA}$ , respectively. Montano *et al.* [11] observed a small contraction in the Ag-Ag interatomic distances for smaller Ag particles by EXAFS analysis. This is consistent with our results because the Ag particle size is smaller in sample Ag-6 than in sample Ag-7. This is further demonstrated by a larger Debye-Waller factor (DWF) for nearest-neighbor Ag-Ag coordination in sample Ag-6 than in sample Ag-7 because smaller Ag particles have larger DWF due to an increasing disorder of surface Ag atoms.

In summary,  $\text{Ag}^+$  ions in soda aluminosilicate glass are coordinated by two oxygens and the Ag-O distance increases when the  $\text{Ag}^+$  for  $\text{Na}^+$  ion-exchange ratio is larger than 0.47. When the exchange ratio is low, the introduced  $\text{Ag}^+$  ions are stabilized at the non-bridge oxygen sites with a Ag-O distance of 2.20  $\text{\AA}$ , and the  $\text{Na}^+$  ions in  $\text{AlO}_4$  sites are exchanged by  $\text{Ag}^+$  ions after full replacement of NBO sites with a Ag-O distance of 2.28  $\text{\AA}$ . The disorder of Ag-O coordination increases with increasing ion-exchange ratio in soda aluminosilicate glass where  $\text{Ag}^+$  ions are coordinated

by NBO and BO. Besides Ag-O coordination, Ag clusters form in soda-lime silicate glass due to the existence of  $\text{Fe}^{2+}$ , and subsequently thermal treatment induces growth of Ag clusters. A small contraction was observed in the Ag-Ag interatomic distances for smaller Ag clusters.

## ACKNOWLEDGMENTS

Supported by Special Funds of Nanotechnology (0452nm075) and Key Project for Basic Research (05JC14058), Science and Technology Committee of Shanghai municipal government.

## REFERENCES

1. E.M. Vogel, *J. Am. Ceram. Soc.* **72**, 719 (1989).
2. V.P. Drachev, A. Buin, K.H. Nakotte and V.M. Shalaev, *Nano Letters* **4**, 1535 (2004).
3. F. Gonella and P. Mazzoldi, in *Handbook of Nanostructured Materials and Nanotechnology*, H.S. Nalwa, ed. (Academic) vol. **1**, p 81 (2000).
4. P.W. Wang, L.P. Zhang, Y. Tao and C. Wang, *J. Am. Ceram. Soc.* **80**, 2285 (1997).
5. X.C. Yang, M. Dubiel, S. Brunsch and H. Hofmeister, *J. Non-Cryst. Solids* **328**, 123 (2003).
6. X.C. Yang, T.L. Du, H. Hofmeister, M. Dubiel and W. Huang, *J. Chin. Ceram. Soc.* **33**, 1371 (2005).
7. S.N. Houde-Walter, J.M. Inman, A.J. Dent and G.N. Greaves, *J. Phys. Chem.* **97**, 9333 (1993).
8. D.A. McKeown, G.A. Waychunas and G.E. Brown Jr, *J. Non-Cryst. Solids* **74**, 325 (1985).
9. T. Yano, T. Nagano, J. Lee, S. Shibata and M. Yamane, *J. Non-Cryst. Solids* **270**, 163 (2000).
10. S.I. Zabinsky, J.J. Rehr, A.L. Ankudinov, R.C. Albers and M.J. Eller, *Phys. Rev. B* **52**, 2995 (1995).