

Silver/sodium ion exchange in optical glasses: an XAFS study

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Ion exchange is widely used to alter the optical properties of glass for application in emerging optical and photonics technologies (e.g., gradient-index imaging systems, optical waveguides, micro-optic lens arrays). The resultant dopant profile determines focal lengths, optical aberrations, and coupling efficiencies with optical fibers.¹ Several aspects of the ion exchange (i.e. concentration dependent diffusion and presence of certain oxides in the glass compositions) are critical in determining the quality of a given optical component and are thought to be somehow related to glass structure. However, the structural chemistry of this process is far from understood.

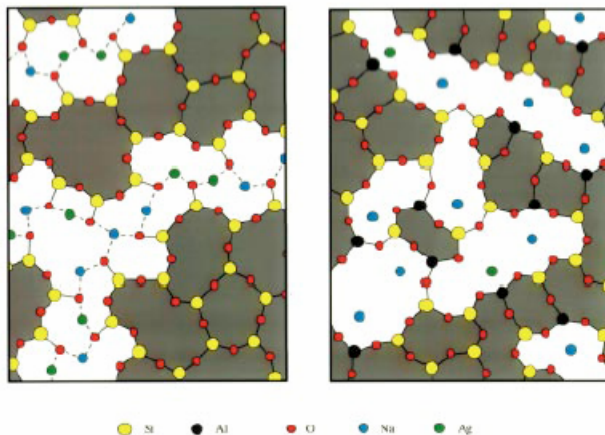
In recent years X-ray Absorption Fine Structure (XAFS) has become a pivotal technique in determining local environments in multicomponent glasses. Early XAFS results lead to the notion that in simple sodium silicate glasses, alkali ions form clusters or channels that are interlaced

throughout the silicate former matrix.² Ion exchange is expected to occur primarily through such channels and the measured atomic environments of alkali and network forming cations have recently been used to predict alkali ion transport properties in binary silicate glasses.³

We recently conducted a study on Ag/Na ion exchange in aluminosilicate glasses in collaboration with G. N. Greaves. The glass compositions and Ag/Na ion exchange pair are representative of those used in the fabrication of commercial optical waveguides and gradient-index optical components. We single out aluminosilicate glasses because alumina (Al_2O_3) has a profound effect on glass properties. For example, the diffusivities of mobile cations improve as Al_2O_3 is added to the alkali silicate glasses, reaching maximum values when the relative concentration $R = [mol\% Al_2O_3] / [mol\% Na_2O]$ is unity. Good chemical durability and suppression of metallic colloid during

ion exchange with silver also result from the addition of alumina in silicate glass melts. As diffusion rates, chemical durability and colloid formation are all fundamentally linked to the behavior of modifier cations, one can expect to observe underlying structural changes in the cation environments as the alumina content of the glass is varied.

We obtained direct structural information on both the constituent (Na^+) and the dopant (Ag^+) cation sites in a variety of silicate and aluminosilicate glasses (compositions listed in Table 1 below) using XAFS on Na and Ag K-edges. We acquired silver K-edge (25.514 keV) transmission data on station A-2 at CHESS shortly before the new wiggler was installed on the A-line. We used the total electron yield technique⁴ to collect data on the sodium K-edge (1.071 KeV) on station 3.4 at the Daresbury Synchrotron Radiation Source (SRS).⁵ Analysis consisted of least-squares fitting of the structure-related parameters to the normalized fine structure using the Daresbury EXCURV90 program,⁶ which is based on curved-wave theory. Procedural details and results can be found in a recent article in the Journal of Physical Chemistry.⁷ First shell determinations are given in Table 2 with an estimated variation in fitted coordination number of ± 0.5 atom, in interatomic distance of $\pm 0.02\text{\AA}$ and in variance of $\pm 0.005\text{\AA}^2$. While overlap exists in the values of N and $2\sigma^2$, it can be seen in Figure 2 that the sodium and silver



(Figure 1) Cartoon of ion-exchanged glass structure: an alkali silicate glass (left) and an alkali aluminosilicate glass (right). Silicon, aluminum and alkali are all 3-fold coordinated in this 2-D representation. The simple alkali silicate glass on the left includes bridging (2-fold) and non-bridging (3-fold) oxygen while the fully polymerized aluminosilicate shown on the right includes only bridging oxygen.

(Table 1) Glass Compositions and XAFS Edges; (R=[mol% Al₂O₃]/[mol% Na₂O]).

Composition	R	Comments	K-edges	
Na ₂ Si ₄ O ₉	0.00	tetrasilicate	Na	Ag
Na _{0.17} Al _{0.05} Si _{0.23} O _{0.58}	0.17	Al ₂ O ₃ -poor; R = 0.17 NAS	Na	Ag
Na _{0.17} Al _{0.15} B _{0.04} Si _{0.09} O _{0.56} ¹¹	0.92	Al ₂ O ₃ -rich; R = 0.92 NAS	Ag	Ag

environments are in fact distinct from one another. The figure gives a comparison of parameter correlation maps⁹ of Debye-Waller factor, $2\sigma^2$, and coordination number, N, for first shell fits on the Na and Ag environments in the glasses listed in Table 1. In each case the first shell $2\sigma^2$ and N were varied to find the region in which the least-squares fit index differed from its minimum by no more than 5%. The parameter range that corresponds to a 95% confidence limit is enclosed by a heavy oval contour. It is obvious that despite the usual uncertainty associated with fitting correlated parameters for a single spectrum, the Na and Ag environments are distinct in all cases.

Sodium environments in silicate and aluminosilicate glasses

Crystalline binary sodium silicates are comprised of sheets of covalently bound silica tetrahedra, separated by soda-rich layers which depolymerize the network. The distinction between the trisilicate and disilicate species lies primarily in the number of silica sheets between the soda-rich layers.⁹ This also appears to be true for the glassy sodium binary silicates. We found that the local Na environments in sodium tetrasilicate (Na₂Si₄O₉) glass are virtually indistinguishable from those previously found² in sodium disilicate (Na₂Si₂O₅) glass. However, the addition of even small amounts of alumina changes the Na environments, as is seen in the R=0.17 glass (Table 2). While the Na-O distance is essentially unchanged, the coordination drops from 4.3 to 2.8 and the static disorder increases significantly.

The change in Na environment can be understood by consideration of crystalline albite (NaAlSi₃O₈). Albite is an open aluminosilicate net-

work in which both Si and Al are four fold coordinated by oxygen to form tetrahedra arranged as three-dimensionally interconnected cages. All oxygen in this crystalline structure "bridge" between either Si or Al cations through covalent bonds. The negative [AlO₄]⁻ groups are charge compensated by Na⁺ ions which occupy the oxygen-rich cages off-center. Similar features can be expected in aluminosilicate glasses.

In glasses with equal parts Al₂O₃ and Na₂O (R=1), the Na⁺ cations can be envisioned as "stuffing" the oxygen rich cavities of the fully-polymerized former network. On the other extreme, in binary glasses (R=0), the Na⁺ cations are tethered to the silicate network through non-bridging oxygens (NBO's). The distinction is shown in the cartoons (Fig. 1) of two 2-dimensional ion-exchanged glasses: a binary silicate for which R=0 and an aluminosilicate for which R=1. The modifier cations are colored Na⁺ (blue) and Ag⁺ (green). Bridging and non-bridging oxygen (both yellow) are distinguished by their coordination to surrounding cations. Note that the binary silicate contains both types of oxygen, while the R=1 glass contains only bridging oxygen. In the R=1 glass, the clustering of alkalis that is present in the binary silicate is essentially absent.

Further, the bridging oxygen cavities are such that the alkali sites generally fall off-center. The difference in the Al-O and Si-O distances (1.7 Å and 1.6 Å, respectively) and the extra disorder in the alkali sites that results is not obvious from the cartoon. In aluminosilicate glasses for which 0 ≤ R ≤ 1, some combination of the two extreme structures can be expected. Evidence for this is seen in Table 2.

Silver environments in the same glasses after Ag/Na ion exchange

Ion exchange usually involves a one-for-one substitution of an alkali ion (e.g., Na⁺) from the glass by a monovalent dopant cation (e.g., Ag⁺). The common assumption is that the dopant makes an isostructural replacement of the constituent.¹⁰ However, we found the Ag environment in the ion-exchanged tetrasilicate glass to be remarkably different than that of the Na which it replaces. In the tetrasilicate glass, the cation coordination number drops from 4.3 (Na-O) to 2.1 (Ag-O) on ion exchange, the distance shortens from 2.32 Å (Na-O) to 2.08 Å (Ag-O) and the Debye-Waller factor sharpens from a $2\sigma^2$ value of 0.017 Å² (Na-O) to 0.012 Å² (Ag-O). The local Ag environment is very similar to our determination of the Ag environment in crystalline Ag₂O: two oxygen at 2.04 Å with $2\sigma^2 = 0.008$ Å². The differences are certainly not due to the presence of metallic colloid since the Ag-Ag distances in silver metal occur at 2.89 Å; these did not feature in the XAFS spectra. The change in oxygen surround can be interpreted in terms of the higher field strength of the silver, the increased covalency of the Ag-O bond and the relative ease with which the mostly ionic NBO/modifier cation bonds can bend. Similar results are obtained for the Ag environments in the low alumina glass in which NBO's predominate the modifier cation sites.

In the alumina-rich (R=0.92) glass, virtually all modifier cation sites will be associated with bridging oxygen. The change in the silver environment (oxygen distances increase from 2.08 Å (R=0) to 2.23 Å (R=0.92), coordination numbers increase from 2.1 (R=0) to 2.5 (R=0.92) and Debye-Waller factors rise from

(Table 2) First Shell XAFS Fits

Glass	Cation	Coordination Number, N	Shell Radius r_{1st} [Å]	Debye-Waller Factor, $2\sigma^2$ [Å ²]
sodium disilicate	Na	5	2.30	0.011
sodium tetrasilicate	Na	4.3	2.32	0.017
	Ag	2.1	2.08	0.012
$R = 0.17$ NAS	Na	2.8	2.30	0.024
	Ag	1.8	2.11	0.018
$R = 0.92$ NAS	Ag	2.5	2.23	0.036

0.012Å² to 0.036Å²) reflects the new constraints experienced by the silver in the stiff, fully-polymerized network. The bridging oxygen bonds are not so free to bend as are the NBO bonds in low alumina glasses, and the silver is unable to pull nearby oxygen into its preferred Ag₂O-like configuration. Instead, the silver must conform to the available oxygen distances in the relatively rigid network and it therefore is accommodated in the network by a higher coordination number and greater local disorder. Incidentally, these fully polymerized aluminosilicate glasses are exactly the compositions used to inhibit formation of metallic silver colloid in ion exchanged glasses.

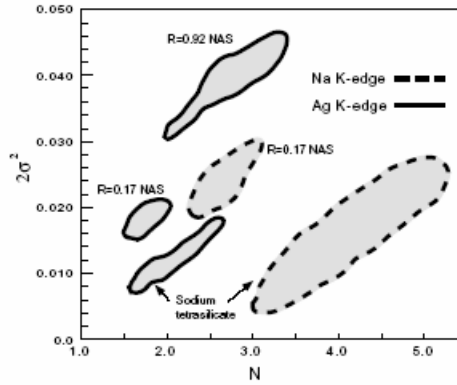
Ionic Diffusion and Ion Exchange

The different environments of the dopant and constituent cations have important implications for ion exchange. For example, relative silver and sodium diffusion rates can be inferred from structural information in these glasses. The electrostatic binding energy E_b for an isolated alkali is given by

$$E_b = \frac{1}{4\pi\epsilon_0\epsilon_\infty} \frac{e^2}{r_{M-O}} \quad (1)$$

where ϵ_∞ is the high frequency dielectric constant and r_{M-O} the alkali-oxygen distance which can be obtained from XAFS. Compared to the host sodium sites, the shorter Ag-O bonds and consequently larger Coulomb forces on the silver indicate that the binding energy, E_b is larger for silver than for sodium, so slower diffusion rates can be expected. This is born out by experiment at all temperatures of interest. For example, the

(Figure 2) Superimposed correlation maps of Debye-Waller factor versus coordination number for first shell fitting to obtain the parameters for the glasses listed in Table 2: (1) sodium in sodium tetrasilicate, (2) sodium in the $R = 0.17$ aluminosilicate, (3) silver in ion-exchanged sodium tetrasilicate, (4) silver in the $R = 0.17$ aluminosilicate and (5) silver in the $R = 0.92$ aluminosilicate glass. The region of 95% confidence is given. The sodium environments group to the right and the silver environments to the left. Note the distinction between environments of the same cation in different glasses (e.g. $R=0, 0.17, 0.92$) and between different cations in the same glass.



silver diffusion coefficient is 4 times smaller than that of the sodium in the $R = 0.17$ glass at typical diffusion temperatures ($T @ 500^\circ\text{C}$).¹¹ In terms of the hopping of isolated cations, we can express the diffusivity ratio, D_{Na}/D_{Ag} at a given temperature as

$$\frac{D_{Na}}{D_{Ag}} = \frac{R_{Na}^2 v_0(Na)}{R_{Ag}^2 v_0(Ag)} \exp\left(\frac{E_b(Ag) - E_b(Na)}{kT}\right) \quad (2)$$

where R_{Na} and R_{Ag} are the respective hopping distances, $v_0(Na)$ and $v_0(Ag)$ the corresponding hopping attempt frequencies and the cation binding energies $E_b(Na)$ and $E_b(Ag)$ are given by eq. 1. Since the glass network is common to both cations, it is reasonable to expect that $v_0(Na) \approx v_0(Ag)$ and that the frequency dielectric constants, $\epsilon_\infty(Na)$ and $\epsilon_\infty(Ag)$, are also approximately equal. If we assume further that the hopping distances R_{Na} and R_{Ag} scale with the respective nearest neighbor oxygen distances, then eq. 2 is simply a function of r_{Na-O} and r_{Ag-O} . Inserting the measured r_{Na-O} values from Table 3 in eq. 1 gives a host to dopant diffusivity ratio D_{Na}/D_{Ag} of 3 - close to the observed value of 4.

The unequal mobilities of the host sodium and exchanged silver cations results in concentration-dependent interdiffusion coefficients, where

$$\frac{1}{\bar{D}} = \frac{N_{Na}}{D_{Ag}} + \frac{N_{Ag}}{D_{Na}} \quad (3)$$

and N_{Na} and N_{Ag} are the cation mole fractions. \bar{D} for ion-exchanged glass de-

pend on silver concentration in a manner completely analogous to the Mixed Alkali Effect.^{11,12} This effect is manifest by low ionic conductivities in mixed alkali glasses compared to those in the single alkali counterparts. The increase in activation energies for ionic conduction have been attributed to alkali-alkali interactions at short distances.¹³ Therefore, the fundamentally different structures of the NBO-rich silicates and the fully polymerized alumina-rich glasses should result in different levels of concentration dependence. For example, in binary silicates one would expect strong cation-cation interactions resulting from the coordination to NBO's on the modifier sublattice. In the fully polymerized glasses (R=1), the concentration dependence should be less pronounced.

We recently tested this hypothesis at the University of Rochester using energy-dispersive x-ray spectroscopic measurements of silver and sodium concentration profiles in ion

exchanged glasses. We find that alumina-rich glasses do indeed show less-pronounced concentration dependence than their NBO-rich counterparts. This is news to both the glass science and the photonics communities and has important implications for the development of new optical glasses. Examples in glass science in which structural knowledge (vs. empirical studies) is used to predict glass properties are rare. This is an encouraging turn of events in the search for better waveguide, micro-optic and gradient-index materials.

Acknowledgments

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