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Computer generated random network models of ion exchanged glasses

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Abstract

Structural models of sodium silicate glasses with reference to silver–sodium ion exchange have been created on the basis of an extended X-ray absorption fine structure study. A random network model derived from the crystal structure of α-$Na_2Si_2O_5$ was generated by successively converting sixfold rings into fivefold and sevenfold rings, while maintaining the SiO_4 tetrahedra. Silver was introduced by substituting for sodium, according to the glass composition. A relaxation of the glass structure was performed using pair and multibody potential functions. By comparison of the experimentally obtained correlation functions with the calculated ones, the assumption was confirmed that the ion exchange causes structural rearrangements within the short range order, as well as attractive Ag–Ag interactions, well below the glass transformation temperature.

1. Introduction

The experimental investigation of glass structure can only give limited information on the arrangement of individual atoms. Therefore, models must be generated to enable an interpretation of the glass structure that is consistent with the experimental data.

This paper is based on extended X-ray absorption fine structure (EXAFS) studies of sodium silicate glasses that were subjected to a Ag/Na ion exchange. The results indicate rearrangements of the local environment of the silver atoms occurring well below the glass transformation temperature [1,2]. A similar behaviour has been reported in the literature for completely different glass compositions (e.g., boroaluminosilicates, sodium tetrasilicates and aluminosilicates) and process parameters [3,4]. These findings are explained by different sodium bonding as well as by the structural relaxation induced by the silver incorporation. Since, until now, no complete microscopic model of ion exchanged sodium silicate glasses is available, random network models of the glass before and after a silver–sodium ion exchange have been generated to interpret the corresponding EXAFS data.

2. Results

2.1. EXAFS measurements

Multi-component sodium silicate glass specimens with 13.8 mol% Na_2O and 72 mol% SiO_2 as the

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main constituents were subjected to Ag/Na ion exchange in a mixed silver–sodium nitrate liquid at 330°C for 310 h. EXAFS experiments at the Na K-edge were carried out at the Synchrotron Radiation Source at the Daresbury Laboratory. The results [2] show that the sodium environment consists of approximately five oxygen atoms at 2.1(8) Å for the pure glass. This result agrees with the short range order in crystalline sodium disilicate and is similar to that of comparable sodium silicate glasses [5]. The incorporation of silver does not lead to drastic changes of the sodium environment; only a slightly increased Na–O bond length occurs together with a small drop in the co-ordination number.

The Ag K-edge spectra were recorded at the VEPP-3 storage ring in Novosibirsk [1,2]. In the case of silver, the nearest neighbour shell consists of two oxygens around 2.1(0) Å which is similar to that for the crystal structure of Ag_2O. The Ag–O distance seems to be essentially constant at different silver concentrations. These results clearly show the difference of the oxygen coordination of sodium and silver, while the other glass regions remain unchanged. Further, a second peak occurs in the Fourier transformed EXAFS function between 2.64 Å and 2.70 Å [1,2]. This peak is a superposition of different pair correlation functions, with the main contribution attributed to Ag–Ag interactions.

2.2. Sodium silicate glass models

There are various routes to build random network models of sodium silicate glasses, e.g., by molecular dynamics simulations (see, for example, Ref. [6]) or by inserting Na_2O in amorphous silicon structures [7]. This work involves the creation of defects in α-$Na_2Si_2O_5$. By means of the molecular simulations program package, CERIUS, a supercell consisting of 1152 atoms was established. Defects were introduced into the crystal structure to eliminate the long-range order of the crystal lattice. The advantage of this method is that particular atomic bonds and structural units, such as the tetrahedral coordination of silicon or the Na–O (NBO) interaction, may be maintained irrespective of the actual potential function applied. The aim of the present approach is to create by rearranging the silica tetrahedra a continuous random network.

In the disilicate crystal lattice, there are only silica tetrahedra with three BOs and one NBO (denoted by Q^3) that are arranged in sixfold rings [8]. The introduction of defects by bond modifications is achieved as follows. First, a pair of silica tetrahedra connected by a bridging oxygen is selected at random. A defect is then created by breaking a NBO bond at one and a BO bond at the other SiO_4 unit, whereby the connecting Si–O–Si bond has to be preserved. New bonds are finally built by exchanging the broken connections. By this procedure two sixfold rings are converted into a fivefold and a sevenfold ring. The model generation was continued until a Q^n distribution of 11.3% Q^2, 74.6% Q^3 and 14.1% Q^4 was achieved which is equivalent to the presence of 18% fivefold, 64% sixfold and 18% sevenfold rings in the network, respectively.

To minimize the energy, the atomic models obtained by defect formation were subjected to a relaxation process by the conjugate gradient method, using a harmonic potential to describe the Si–O and Na–O interactions in the first co-ordination sphere, and the body term to calculate the O–Si–O, Si–O–Si, and Si–O–Na bond bending potentials. Further interactions as well as higher pair correlations (Na–Na, Na–Si, Na–O) were described by Lennard-Jones

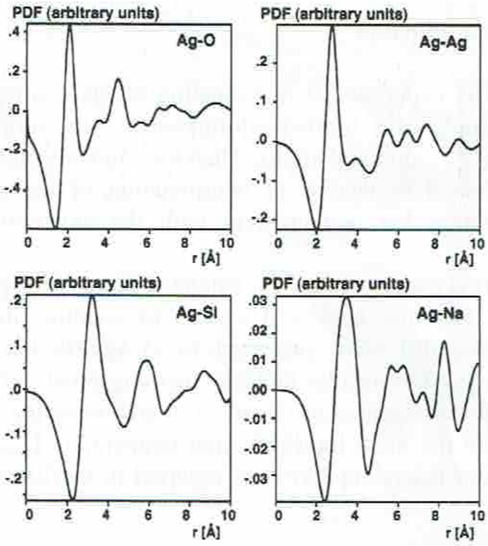

Fig. 1. Partial pair correlation functions (PDFs) for silver determined from the silver containing glass model (80% Ag/Na exchange ratio).

potentials or a repulsive force of exponential form. The peaks of the pair correlation function can be assigned to the corresponding distances (Si–O: 1.63 Å; Na–O: 2.38 Å; O–O: 2.62 Å; Si–Si: 3.10 Å; Si–Na: 3.38 Å; Na–Na: 3.65 Å).

2.3. *Silver incorporation into the models*

Various proportions (20, 50 and 80%) of the sodium atoms in the model structure were randomly replaced by silver using a Monte Carlo method. The other structural parameters, in particular the ring size, distribution of Q^n species, bond parameters, co-ordination numbers, etc., remain unchanged during this exchange. To allow a conversion of the oxygen environment of the cations, a further relaxation was performed by introducing additional pair correlations specific to silver.

For Ag–O (NBO) bonds an enhanced degree of covalency is expected [3]. Therefore, a harmonic potential is employed with an equilibrium Ag–O distance chosen according to the EXAFS data, and an increased bond-stretching constant as compared with the Si–O and Na–O bonds. The Si–O–Ag bond bending term is chosen to 110°. The Ag–Si and Ag–Na interactions, described by the same repulsive potential as used for the corresponding sodium bonds, are applied with identical parameters. The Ag–Ag correlation below 3 Å as found by EXAFS could be realised by a Lennard-Jones potential. In addition to the Ag–O bond to the corresponding non-bridging oxygen atom, further Ag–O interactions with attractive components must be included, to achieve the experimentally observed twofold oxygen co-ordination. This was also achieved by Lennard–Jones terms. The resulting pair correlation functions for silver are represented in Fig. 1.

3. Discussion

The behaviour of the calculated distribution function for the disilicate glass is comparable with that of other simulations and experimental results [6]. A slight increase of the Na–Na separation is obtained since only potentials with repulsive terms to avoid sodium clustering were used. Nevertheless, the generated structure is a realistic glass model and well suited to studying the incorporation of silver.

Comparing the structural configurations as given by individual pair correlations before and after the ion exchange, it may be recognized that only the cation environments have been rearranged. Table 1 gives a survey of the most important correlations at various exchange ratios derived from the model and estimated from the experiments, respectively. The Ag–O distance in the model exhibits an average value of 2.04 Å, having a slight tendency to decrease with increasing silver content. This is in good agreement with the experimental findings [2]. The Na–O distance in the model shows no change throughout the range of silver concentrations applied. The deviation from the experimentally obtained values may result from both the limited accuracy of the bond length determination (5%) and the difference between the sodium content of the model (33 mol%) and that of the glass sample (14 mol%) studied. The experimentally estimated (2.64–2.70 Å) and the model (see Fig. 1) values for the Ag–Ag distance are similar to the bond length in binary and ternary

Table 1
Comparison of the cation environment estimated from EXAFS spectra [2] and that derived from the glass model. The experimental error for EXAFS data is given in parentheses

Exchange ratio (%)	Na–O			Ag–O		
	distance (Å)		coordination	distance (Å)		coordination
	exp.	model	model	exp.	model	model
20	2.2(2) [a]	2.37	3.7	2.0(0) [a]	2.07	2.1
50	2.3(5) [a]	2.37	3.7	2.0(6) [a]	2.03	2.3
80	–	2.37	4.0	2.0(0) [a]	2.02	2.3

[a] These parameters are determined experimentally at slightly different exchange ratios.

silver oxides, such as Ag_6O_2 (2.75 Å) [9] or $Ag_4Si_2O_7$ (2.95 Å) [10].

4. Conclusions

The generation of three-dimensional atomic models of sodium silicate glasses by successively introducing defects into crystalline sodium disilicate has been shown to be appropriate for studying ion exchange. The random replacement of sodium by silver, accompanied by relaxation according to a set of potential functions, leads to a rearrangement of the cation environment. No transformation of the basic structural units is required to achieve these results. The Ag–O environment with the shortened bond lengths and the twofold oxygen coordination is unambiguously related to the increased covalency of this bond. Additionally, an attractive force between the silver ions has to be considered to establish the observed Ag–Ag distances after the ion exchange. On the basis of structural investigations of various crystalline silver compounds [11], these Ag–Ag correlations are attributed to homoatomic interactions between closed d^{10} shells.

The present results allow the ion exchange process to be discussed in more detail. It is obvious that the silver ions form their own environment well below the glass transformation temperature, T_g. With regard to diffusion and conduction phenomena, this represents an increased energy barrier for a direct exchange of the sodium and silver ions. The decreased mobility of sodium should effectively prevent a transformation back to a sodium-like environment below T_g; i.e., the ion exchange causes non-reversible changes of the glass structure. Further, the resulting glass structure may serve as a structural basis for modelling the mixed alkali or mixed oxide effect as proposed by Bunde et al. [12].

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