

LNF-90/106

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Estratto da: Conf. Proc. Vol. 25 XSR-89, A. Balerna, E. Bernieri, S. Mobilio (Eds.)
SIF Bologna, Pag. 647 (1990)

XANES AND EXAFS STUDY OF AR AND XE BEARING SiO₂ GLASSES

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ABSTRACT

XANES and EXAFS spectra of the Si k-edge for SiO₂ glass and experimentally synthesized Ar- or Xe-bearing SiO₂ glass show that the glass structure is measurably altered by introduction of ~0.8 wt% Ar and also altered, albeit to a lesser extent, by introduction of Xe in amounts ~0.1 wt%. These differences are most apparent in the XANES spectra although the EXAFS results for the Ar-bearing glass are slightly different from those for the starting material. The data suggest that at high gas contents the assumptions implicit in the Langmuir adsorption model of inert gas solubility in glass must be treated with caution, i.e. the solution process *does* affect the glass structure. These preliminary results indicate that further experiments with glasses of different gas contents, along with spectral simulations are needed to better understand the atomistic-scale changes accompanying dissolution of inert gases in silica glass.

INTRODUCTION

Studies of the solubility and diffusivity of inert gases in silicate glasses and melts can provide information about glass structure and about the microscopic details of how inert gases dissolve in silicates. The observation by numerous workers (e.g. Lux, 1987) that the solubility of inert gases is inversely correlated with the density of the silicate solvent suggests that gas dissolution occurs via an interstitial mechanism and thus SiO₂ glass, with no "extra" cations occupying the spaces between the interconnected (SiO₄) tetrahedra provides a useful end-member case for looking at how gas atom size and solubility mechanism may be related. Of greatest interest are the questions of (1) whether the dissolution of a gas atom is accompanied by any volume change, i.e. are the volumes of an occupied and vacant site identical, and (2) is there any tendency for gas atoms to cluster together, as has been suggested by molecular dynamic simulations of Ar in high temperature melts (Angell et al., 1987) and has been observed in studies of rare gas solids (Malzfeldt et al., 1984). In this contribution we briefly present initial EXAFS and XANES results for the Si K-edge in silica glass containing dissolved Ar or Xe.

METHODS

Samples of SiO₂ glass containing dissolved noble gases were prepared by exposing finely ground silica glass (Heraeus Amersil; Type II silica of Brückner, 1970) to high pressure Ar or Xe in a metal autoclave. The powder samples were enclosed in unsealed Au capsules and put in an autoclave, which was subsequently evacuated to ~10⁻³ atm and then filled to several thousand bars with high purity Ar (99.997%) or Xe (99.99%). The autoclaves were heated using an external furnace with temperature electronically controlled

to within $\pm 5^\circ\text{C}$ as measured by a Chromel-Alumel thermocouple situated in a well in the autoclave, within several mm of the sample. Pressure was measured with a Bourdon tube gauge or with an electronic pressure transducer and is accurate to ± 50 bars. After being held at high pressure and temperature for the desired length of time the autoclave was removed from the furnace and quenched to room temperature within five minutes in a stream of compressed air.

EXAFS and XANES spectra of the Si K-edge of the glass samples were collected at Frascati Synchrotron Radiation Facility using the PULS X-ray line equipped with an InSb crystal monochromator suitable for working at the Si K-edge absorption energy. A millipore filter was used to support the sample in order to minimize as much as possible any extra absorption effects. In the data analysis the pre-edge absorption background was subtracted following the method of Mobilio et al. (1982) and the spectra were normalized to the adsorption value observed at very high energies. The Fourier transforms were calculated using a Gaussian window.

RESULTS

Samples for which EXAFS spectra were taken include the following: (1) AX-0, the SiO_2 glass starting material, (2) AX-68, SiO_2 - ~ 0.8 wt% Ar, formed at 2978 bars Ar, 700°C , 40.85 days, and (3) AX-176, SiO_2 - ~ 0.1 wt% Xe, formed at 2300 bars Xe, 800°C , 4.71 days. The same starting material was used for all experiments. Relaxation times for the starting material are on the order of hundreds of years and thus the differences we observe in the X-ray spectra of the starting material and the Ar- and Xe-bearing samples cannot be due to the slight differences in pressure and temperature of synthesis.

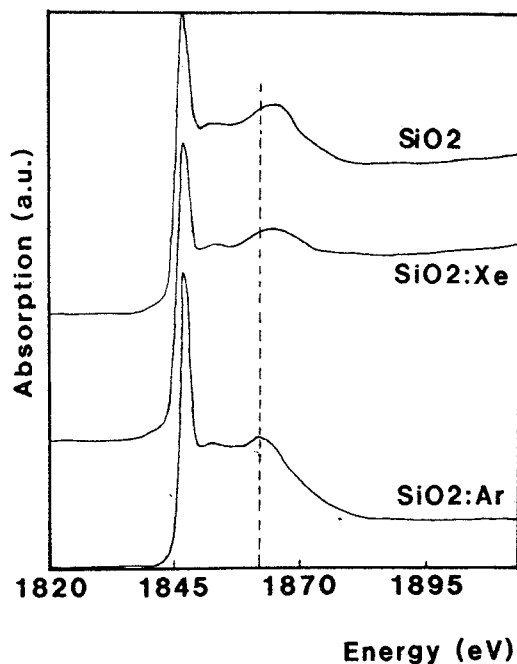


Fig. 1. Si K-edge XANES spectra with dashed vertical line marking peak position for SiO_2 -Ar sample.

The XANES spectra of the Ar and Xe-bearing SiO_2 glasses at the Si K-edge are shown in Figure 1, where they are compared with the pure SiO_2 starting material used as a reference. The greatest difference is seen between the SiO_2 - Ar and the SiO_2 spectra, as might be expected from the higher concentration of Ar in the glass. Despite the difference in intensity, probably due to thickness differences, the 1862 eV peak for SiO_2 - Ar sample is clearly shifted by 3.6 eV toward lower energy compared with the analogous peak in the reference material. This part of the spectrum is characterized by multiple scattering events and is affected by phenomena beyond the pair distribution function. Moreover, the peak position is strongly influenced by the Si-O-Si bridging angle (Davoli et al., 1989) and the observed shift may correspond to an increase in this angle for some of the Si atoms. The SiO_2 - Xe spectrum looks very similar to the reference compound but a comparison between the derivative spectra for these samples (Figure 2) shows that the peak near

1865 eV is also slightly shifted and broader than that observed for pure SiO₂, suggesting a smoothing of the contributions due to the Si-O-O-Si scattering path in the Xe-bearing sample. EXAFS results for the three samples are almost identical and the first nearest neighbor (Si-O) distance is constant (Greaves et al., 1981). However, in the radial distribution function (Figure 3), the SiO₂-Ar Fourier transform shows that a small but detectable modification occurs in shells further than the first, with a 0.2 Å shift of the second peak towards longer distances (relative to reference sample). This suggests that even a small amount of Ar in the glass structure may alter the local environment.

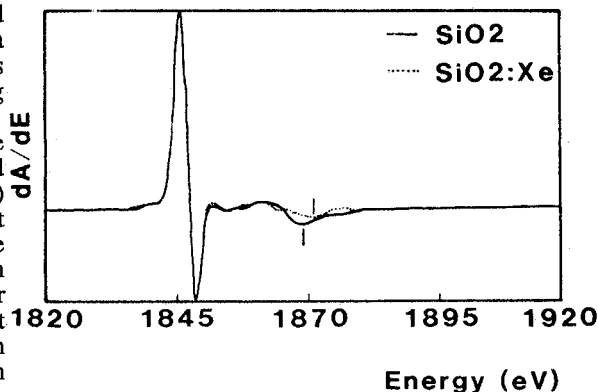


Fig. 2. Derivative spectra for SiO₂ reference sample and Xe-bearing SiO₂.

DISCUSSION

Silica glass can be envisioned as a three dimensional network of corner-shared silicate tetrahedra which define relatively large open spaces or holes that alkali metal ions or noble gas atoms may enter (cf. the crystalline phases cristobalite or tridymite). Barrer and Vaughan (1967) showed that He and Ne solubility in tridymite and cristobalite may be successfully treated by a Langmuir adsorption model in which the gas atoms enter holes in the crystal structure. The Langmuir model has also been applied to gas dissolution in silica glass, and then used to estimate the size distribution of holes in the glass. However, implicit in such treatments is the assumption that the solution process involves no volume change or change in the architecture of the silicate matrix, e.g. Si-O-Si angles. Our XANES and EXAFS results for the Si K-edge of Ar or Xe bearing SiO₂ glass show distinct differences when compared with the gas-free starting material, suggesting that changes in the glass structure due to gas solution may not be negligible. Further experimental work combined with simulations of the spectra already collected will hopefully shed more light on the

changes in glass structure due to dissolved gas atoms. It is possible that solution of the smaller He and Ne atoms is not accompanied by any changes in glass structure while solution of Ar or larger atoms does affect the glass structure.

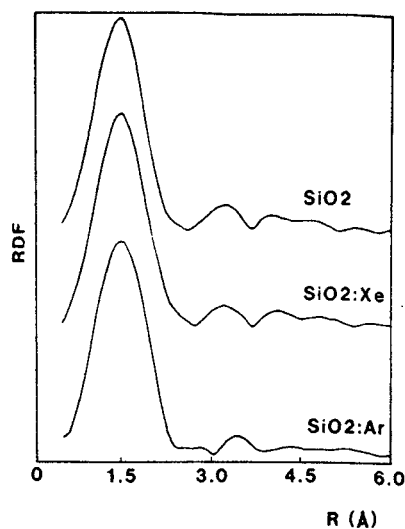


Fig. 3. Radial distribution functions of the investigated samples.

Acknowledgements: This work was partially supported by NASA grants NAG 9-236 and NAGW-1427, and CNR 88.01678.05.

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