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LOCAL STRUCTURE IN SiO_2 GLASSES BY OXYGEN K EDGE XANES

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Résumé Les structures des spectres d'absorption X près du seuil (XANES) K de l'oxygène dans des verres de silices bien caractérisés ont été mesurées sur le synchrotron de Frascati. Le XANES sur l'oxygène est sensible à la géométrie du site de l'oxygène dans le verre. Des calculs de diffusion multiple pour un modèle simple de cluster Si-O-Si ont montré la sensibilité du XANES aux variations des angles entre liaisons, à travers les corrélations d'ordre élevé des fonctions de distribution atomique.

Abstract The X ray absorption near edge structure (XANES) spectra, at the oxygen K edge, of well characterized silica glasses have been measured using the grasshopper beam line at the Frascati synchrotron radiation facility. Oxygen XANES are shown to be a probe of oxygen site geometry of glasses. Multiple scattering calculations of XANES for a simple Si-O-Si cluster have been performed and demonstrate the sensibility of XANES to bonding angles via higher order correlation function of atomic distribution. The feasibility of Si-O-Si bridging bond angle and of Si-O distance determination and indication of different average bridging bond angles in different silica glasses by XANES is reported.

I - INTRODUCTION

Silica glasses are formed by SiO_4 tetrahedral clusters and the disorder is determined by the variation of the Si-O-Si bridging angle at the corner sharing of two tetrahedra. In α -quartz this angle is 143.5° and the Si-O distance is 1.603 \AA ⁽¹⁾ The distribution of the bridging angle is not well defined in Ameril silica glass that has been measured by Mozzi et al. ⁽²⁾ They report an angle distribution between 120° and 180° centered at 144° .

This result has been questioned by Da Silva et al. ⁽³⁾ and further investigations by EXAFS ⁽⁴⁾ and by magic angle spinning NMR ⁽⁵⁾ have been carried out. Extensive neutron scattering studies by Sinclair et al. ⁽⁶⁾ have

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determined the Si-O distance $1.61 \pm 0.01 \text{ \AA}$ and the O-O distance which indicates a regular tetrahedron.

Raman spectroscopy has been used to get structural information on silica glasses and evidence of planar 3-fold rings in concentrations of the order of 1% with small 130.5° bridging angle has been reported.^(7,8) The absence of heterogeneities down to the size of 20 Å has been found by high resolution electron microscopy, however the presence of paracrystalline domains of smaller dimension remains controversial.^(9,10) A recent review on the problem of the structure of silica glass has been made by Kreidl.⁽¹¹⁾

We report the first results on the investigation of well characterized silica glasses by using XANES (X-ray absorption near edge structure) spectroscopy.⁽¹²⁻¹⁷⁾ In a previous work the Si tetrahedral site in amorphous SiO₂ layer has been studied by Si L-edge⁽¹⁶⁾. Here, by measuring the oxygen K-edge spectra, the oxygen site structure is investigated. In fact, by multiple scattering processes, XANES probes higher order correlation functions of atomic distribution around the absorbing atom. Our preliminary results show the sensitivity of XANES to bond angle and bond distance variation at the oxygen site in a 'natural' and a suprasil silica glasses.

II. EXPERIMENTAL

The oxygen soft X ray absorption spectra of quartz and of silica glasses have been measured at the Frascati "grasshopper" beam line. The absorption cross section has been measured by partial electron yield technique. The secondary electrons emitted at 2 eV kinetic energy are selected by a cylindrical mirror analyser and their intensity as function of the photon energy is measured. The samples were held in an ultra-high vacuum system and the spectra were recorded on untreated samples and on sputtered surfaces by argon ion beam. The quartz sample was a very pure natural α -quartz from British Columbia. We guess its total impurity content to be less than 50 ppm. The 'natural' silica glass was prepared by melting a natural brasilian quartz crystal powder at around 2000°C in reducing atmosphere for 20 hours. Its impurity content has been determined by atomic absorption: there are 20 ppm of Al together with 5 ppm of alkali impurities and 3 ppm of transition elements. The OH content is very low: about 1/10 ppm. The third studied sample was a synthetic silica glass with commercial name Suprasil-WII. It is obtained by oxidation of SiCl₄ in a dry flame. This a stoichiometric SiO₂ glass which is virtually free (less than 1 ppm) of metallic and alkali impurities and OH groups (less than 5 ppm), however the amount of halide impurities can be of the order of 100 ppm.

III - RESULT AND DISCUSSION

The XANES spectra of quartz crystal, of the 'natural' and of Suprasil silica glasses are shown in fig.1 The oxygen K XANES shows in all spectra a weak

shoulder on the rising absorption edge, a main line with a shoulder on its high energy side and a broad resonance at about 21eV above the main line. We show here the spectra of sputtered samples. There is a variation going from the crystal to the glass spectra concerning the intensities of the main line and of the resonances at higher energy .

FIG. 1. Oxygen K-XANES of α -quartz , of 'natural' silica glass, and of suprasil WII .

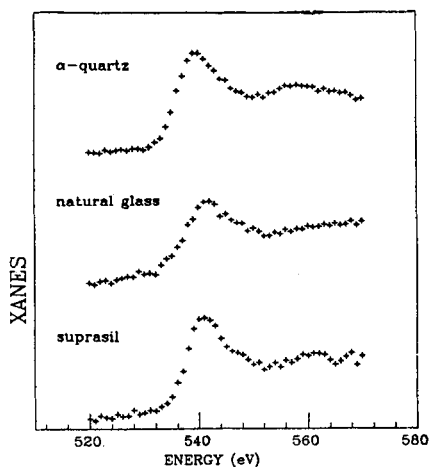
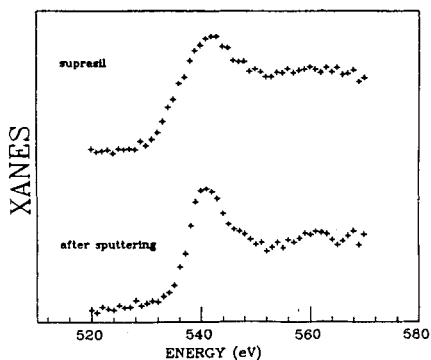


Fig. 2. Oxygen K-XANES of suprasil WII glass before and after argon ion sputtering.



The partial electron yield method is surface sensitive because of the electron escape depth which is estimated to be of the order of 50-100 Å. In fig.2 we report the spectra of suprasil glass of the untreated sample and after ion argon sputtering which exhibits some variations. At this time we cannot conclude if the effect is due to contamination on the untreated surface or to structural modification introduced by sputtering.

The XANES spectra have been interpreted using the multiple scattering

theory⁽¹⁵⁾ for a small cluster formed by the central oxygen atom and two neighbouring Si atoms with different Si-O-Si bridging bond angles. This should be considered a first approximation to understand the physical origin of the observed experimental structures, in fact the contribution of photoelectron scattering from the oxygen atoms in the second shell cannot be neglected. In the energy region where the expansion of the cross section in terms of contributions of multiple scattering pathways which begin and end at the oxygen site (classified according with the number of scattering events $n=2$ (EXAFS), 3, 4, ...) is possible, the total cross section α_t can be factorized into

$$\alpha_t = \alpha_a \left(1 + \sum_{n=2}^{\infty} \chi_n \right)$$

In fig. 3 we report the theoretical spectrum for a simple Si-O-Si collinear cluster $\theta = 180^\circ$. The total and the atomic absorption coefficient are reported in the upper part, while the partial contributions for $n=2, 3, 4, 5$ are in the below panels. In this geometry the higher order contributions ($n=3, 4, \dots$) are very important up to high energy because of strong forward scattering but they are neglected by cancellation effect for a destructive interference. The spectrum shows only one bound state which appears as a weak shoulder on the low energy side of the main line observed also in the experimental data. The main line is a multiple scattering resonance in the full multiple scattering regime below the energy limit $E_c = 0.4$ Ryd, above of which the expansion is possible.

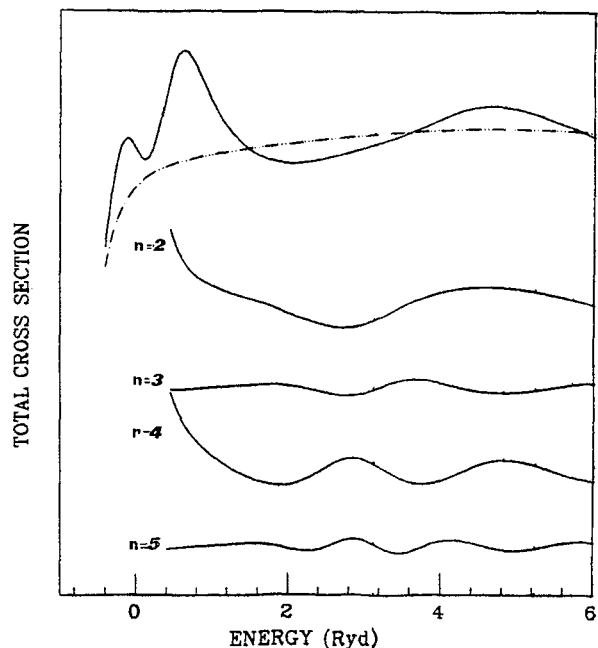


Fig. 3. Multiple scattering theoretical oxygen K-XANES for a simple collinear Si-O-Si cluster with bridging angle 180° . The total and the atomic cross sections are plotted in the upper part, in the lower panels the contributions due to successive orders of scatterings pathways from $n=2$ (EXAFS) to $n=5$ are shown.

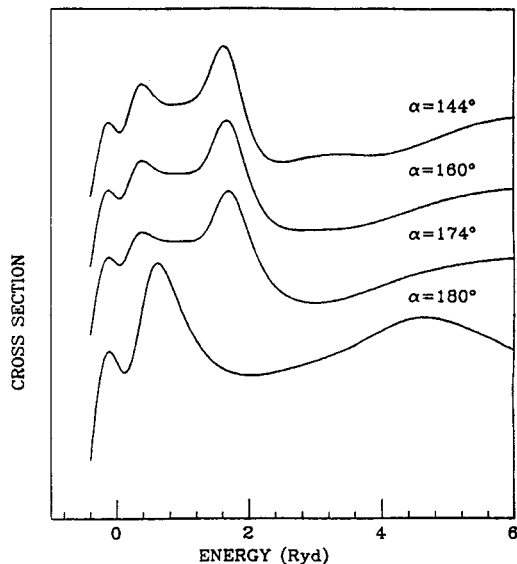


FIG. 4 Total photoionization cross section for oxygen K-edge spectra for a set of Si-O-Si clusters with different bridging bond angles 144° , 160° , 174° and 180° from top to bottom.

The calculations of the total absorption coefficient for a set clusters with different bridging bond angles are shown in fig.4. Going off collinear configuration the destructive interference effect is suppressed. Two multiple scattering resonances (MSR) appear. The agreement with the experiment is poor, showing that it is necessary to take account also of further atoms such as the other six oxygens of the two SiO_4 tetrahedra sharing the central oxygen atom. Theory shows that bridging bond variation induces a change on the intensities of multiple scattering resonances. The effect of bond distance changes are very strong on MSR ⁽¹²⁾ and a blue shift of 1 eV for 0.02 Å contraction of the Si-O distance has been observed.

In conclusion these results show the advances in the measure of geometry of local structure in silica glasses by XANES also if not definitive conclusions can be derived. The experimental spectra in the difficult oxygen K-edge soft X-ray energy range are reported and XANES is shown to be sensitive to the different local structures in the glasses. The theoretical analysis has shown that XANES by probing multiple scattering photoelectron pathways is sensitive to bridging bond angle and distance variations.

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